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Carpenter et al.

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(54) **FUEL INJECTOR NOZZLE**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 352 days.

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(65) **Prior Publication Data**

US 2016/0230732 A1 Aug. 11, 2016

Related U.S. Application Data

(62) Division of application No. 13/387,550, filed as application No. PCT/US2010/043628 on Jul. 29, 2010, now Pat. No. 9,333,598.

(Continued)

(51) **Int. Cl.**

F02M 61/18 (2006.01)
B23P 15/16 (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***F02M 61/1833*** (2013.01); ***B05B 1/06*** (2013.01); ***B23P 15/16*** (2013.01); ***B29C 59/00*** (2013.01);

(Continued)

(58) **Field of Classification Search**

CPC F02M 61/1833; F02M 61/1806; F02M 61/168; F02M 2200/8069; F02M 61/184;

(Continued)

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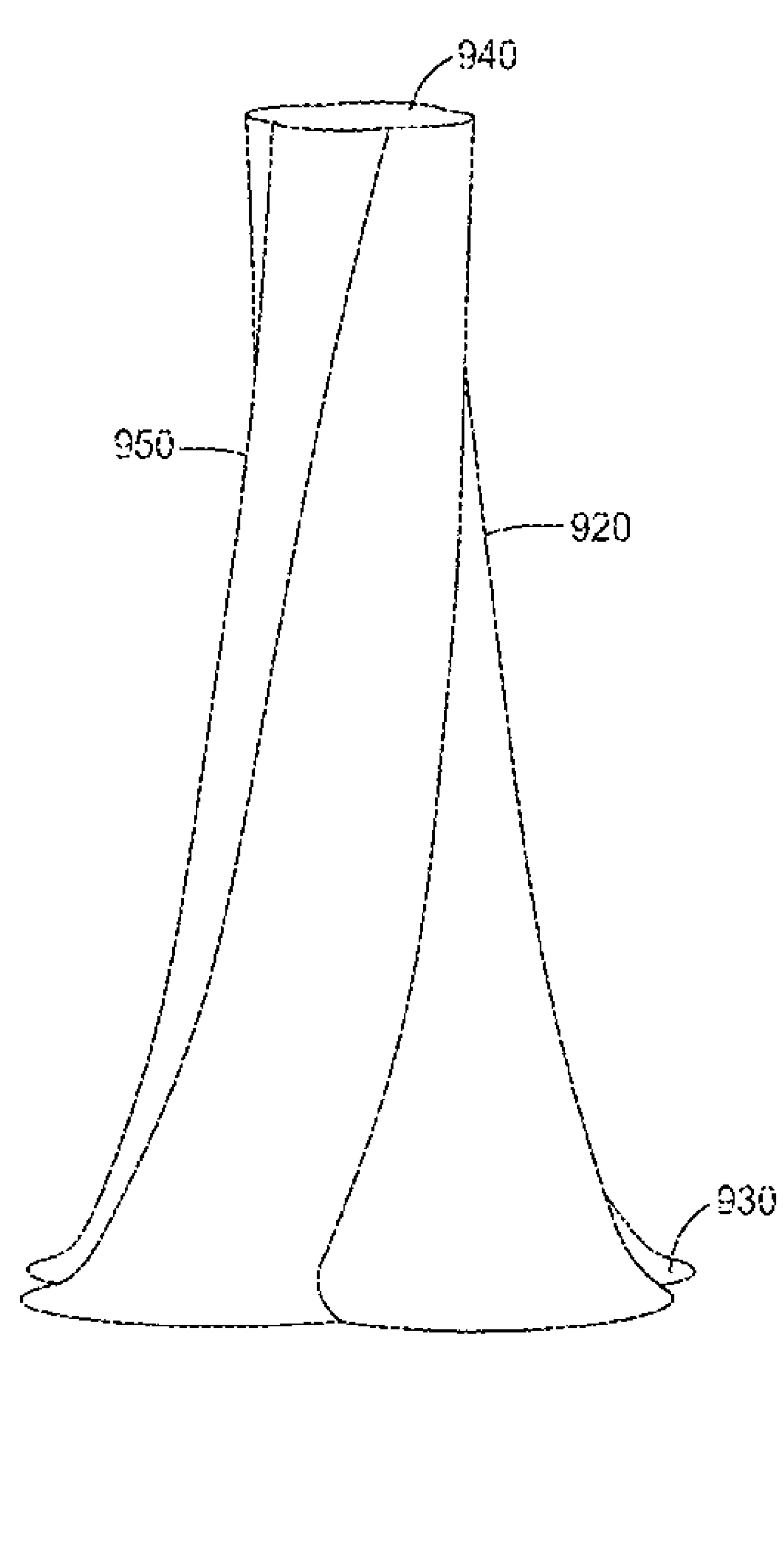
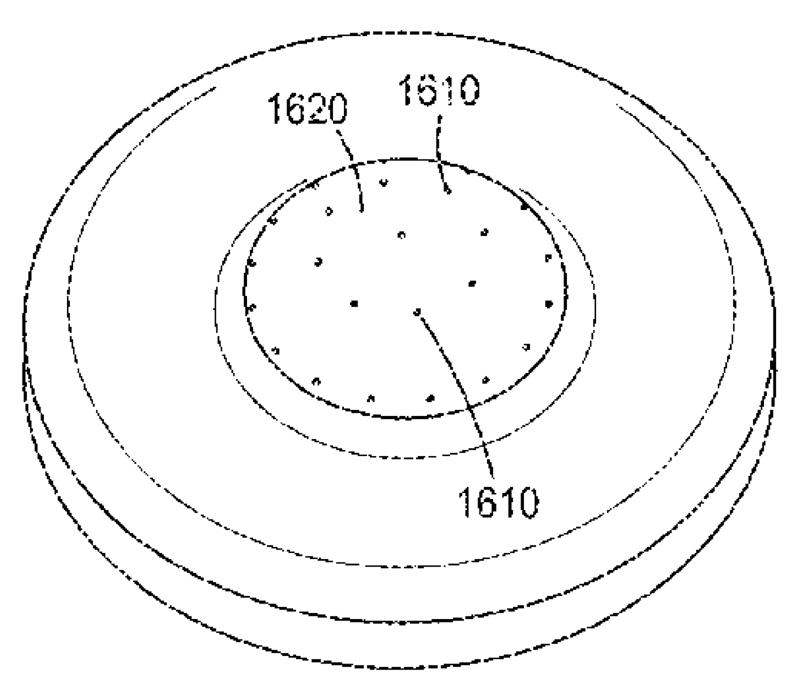
Primary Examiner — Sarang Afzali

(57) **ABSTRACT**

A fuel injector nozzle comprising a plurality of holes formed therethrough connecting one side of the nozzle with an opposite side of the nozzle. Each of the holes comprises a hole entry on the one side of the nozzle having a first shape, a hole exit on the opposite side of the nozzle having a second shape, and a hole wall connecting the hole entry to the hole exit. The hole exit is smaller than the hole entry, and the hole wall comprises a side that is continuously curved from the hole entry to the hole exit.

17 Claims, 20 Drawing Sheets





Related U.S. Application Data

(60) Provisional application No. 61/229,821, filed on Jul. 30, 2009.

(51) **Int. Cl.**

B05B 1/06	(2006.01)
F02M 61/16	(2006.01)
B29C 59/00	(2006.01)
C23C 14/14	(2006.01)
C23C 14/58	(2006.01)
C25D 3/12	(2006.01)
C25D 5/48	(2006.01)
C25D 7/00	(2006.01)

(52) **U.S. Cl.**
CPC ***C23C 14/14*** (2013.01); ***C23C 14/58*** (2013.01); ***C25D 3/12*** (2013.01); ***C25D 5/48*** (2013.01); ***C25D 7/00*** (2013.01); ***F02M 61/168*** (2013.01); ***F02M 61/184*** (2013.01); ***F02M 61/1806*** (2013.01); *F02M 2200/8069* (2013.01); *Y10T 29/49432* (2015.01); *Y10T 29/49433* (2015.01)

(58) **Field of Classification Search**
CPC C23C 14/58; C23C 14/14; C25D 5/48; C25D 3/12; C25D 7/00; B29C 59/00; B05B 1/06; B23P 15/16; Y10T 29/49433; Y10T 29/49432
See application file for complete search history.

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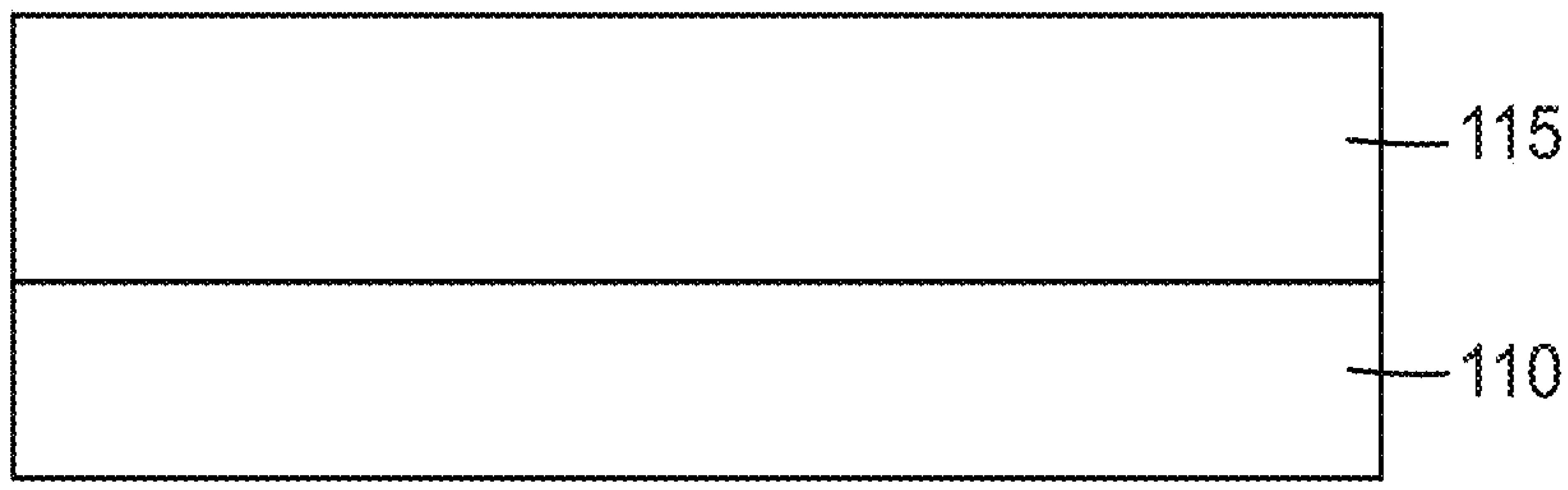


FIG. 1A

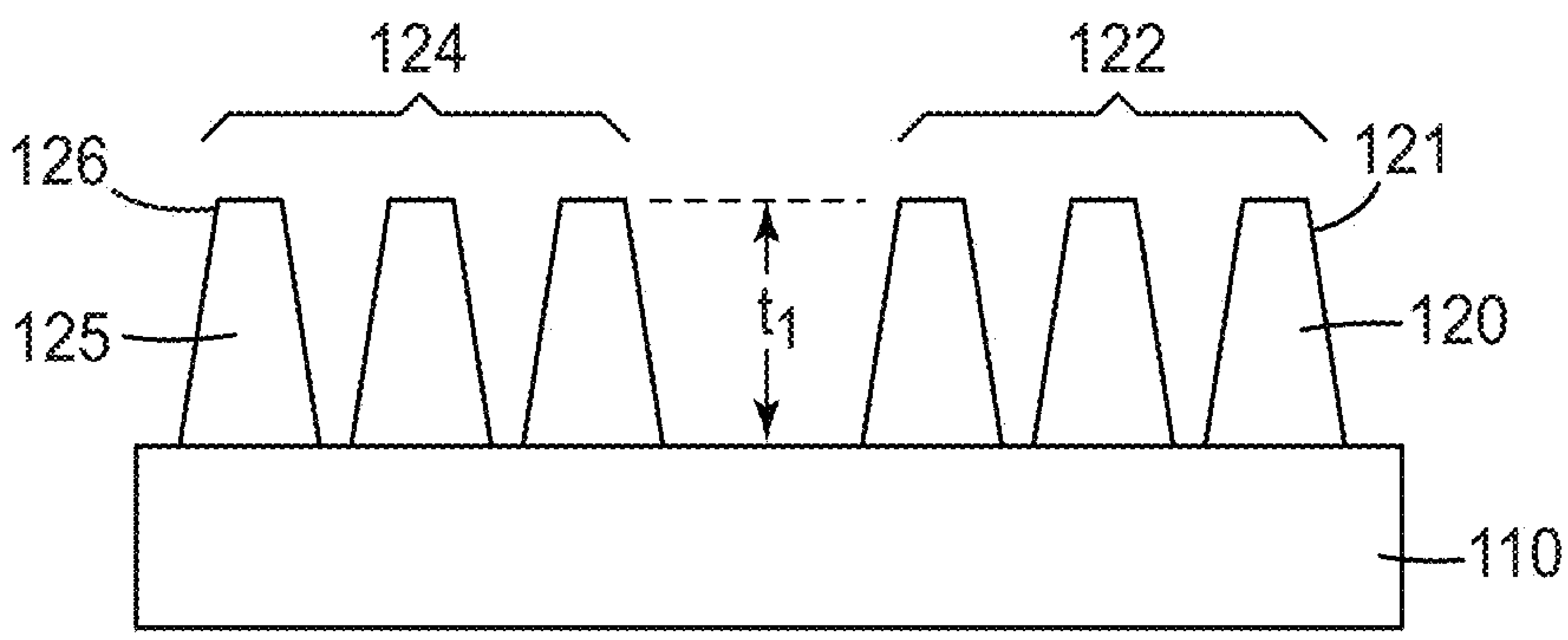


FIG. 1B

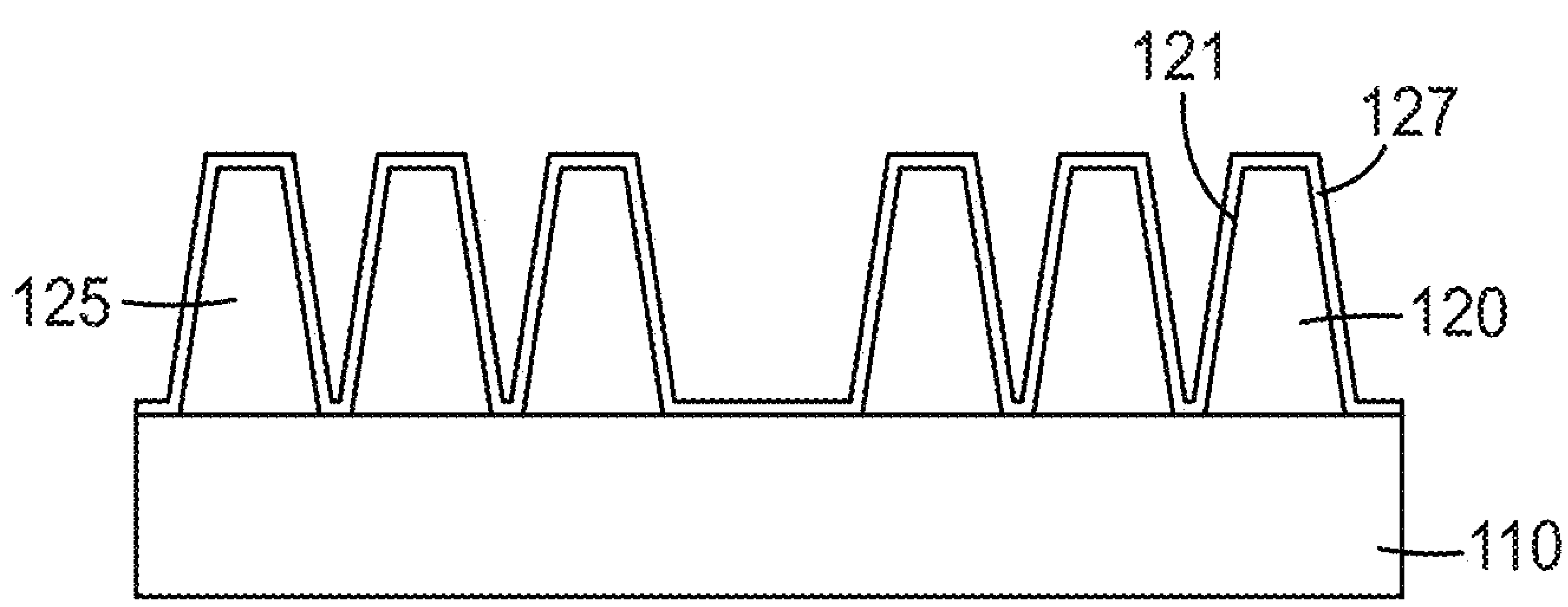
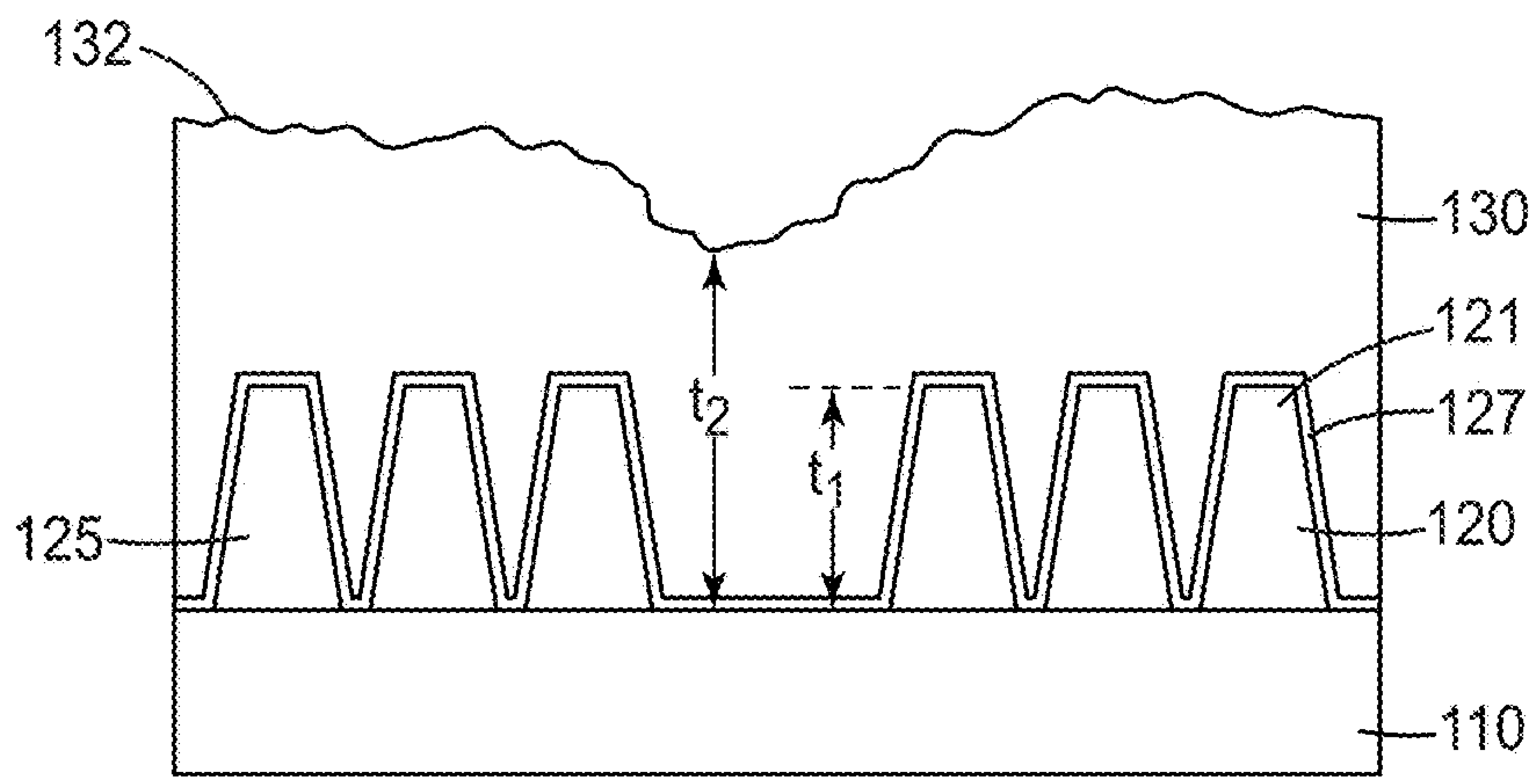


FIG. 1C



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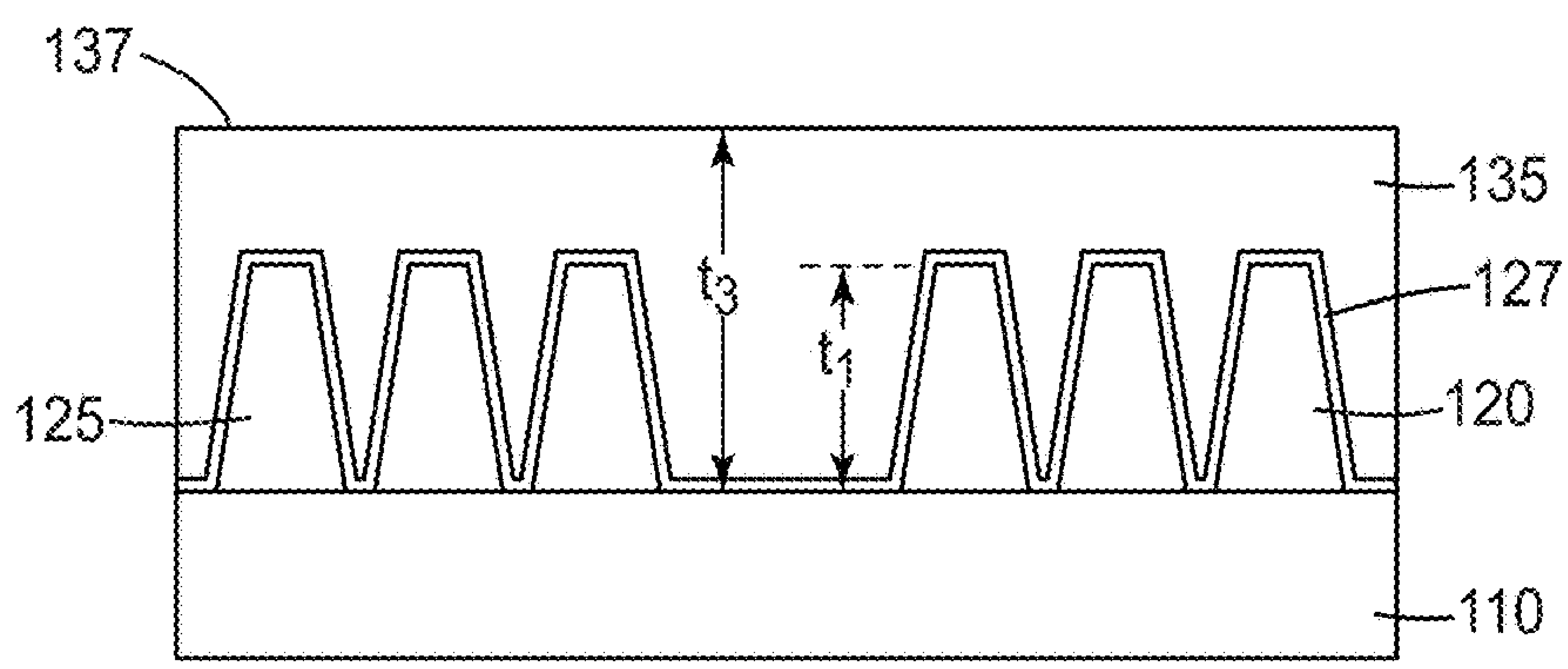

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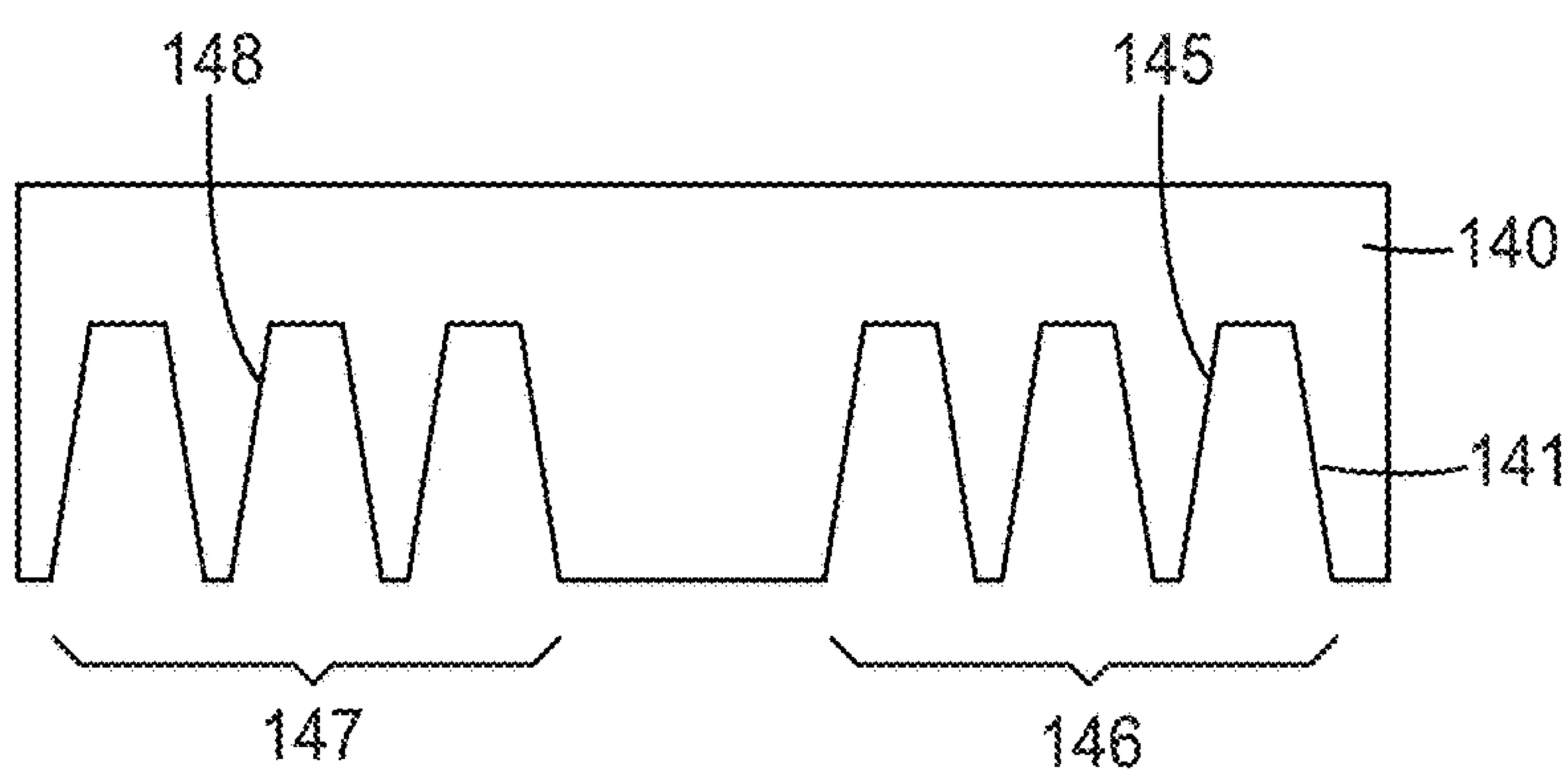

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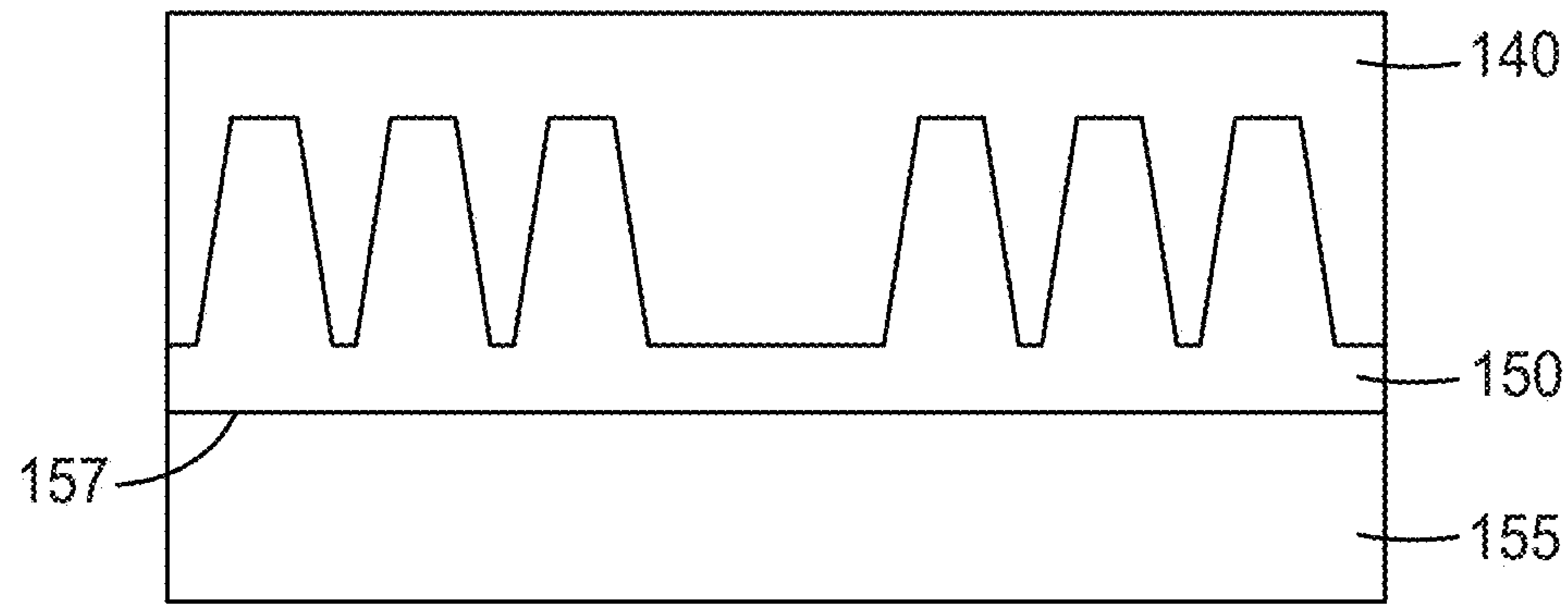

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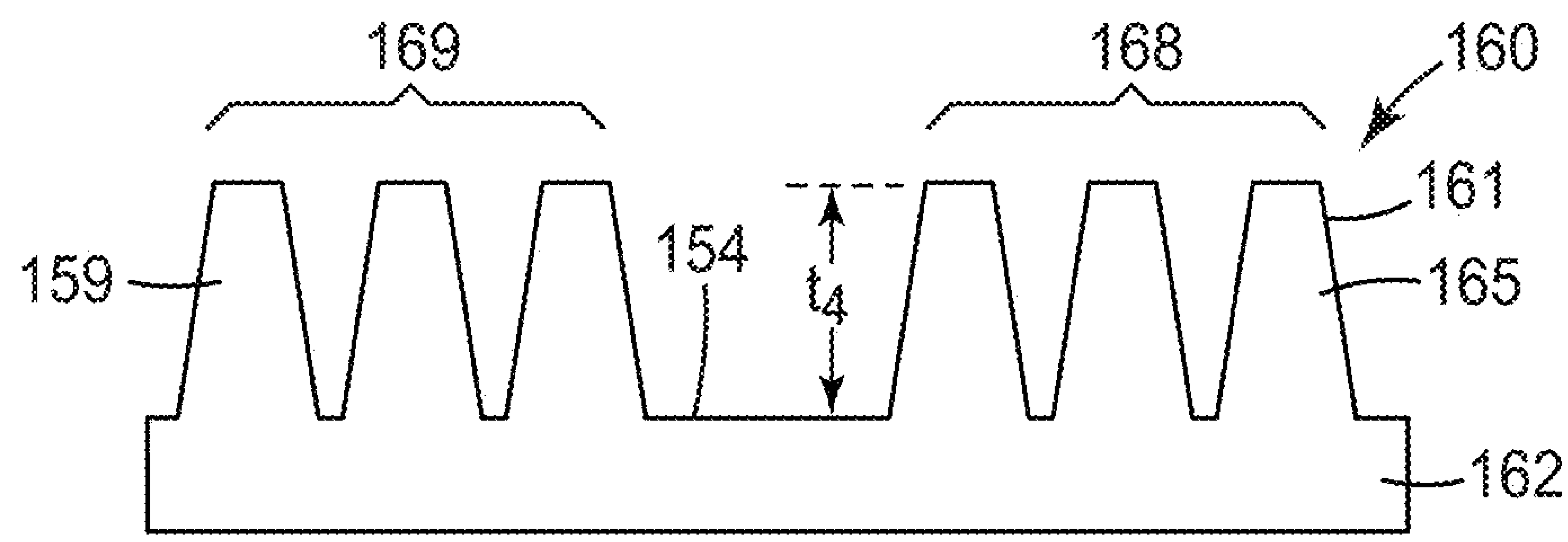

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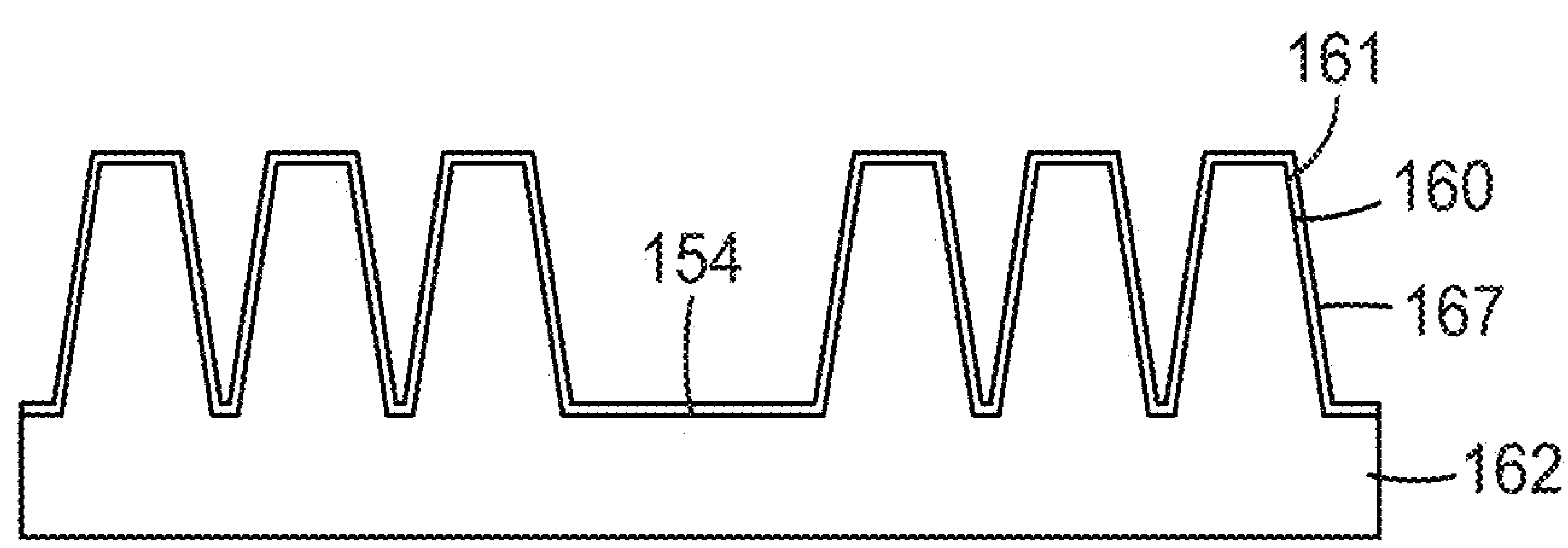
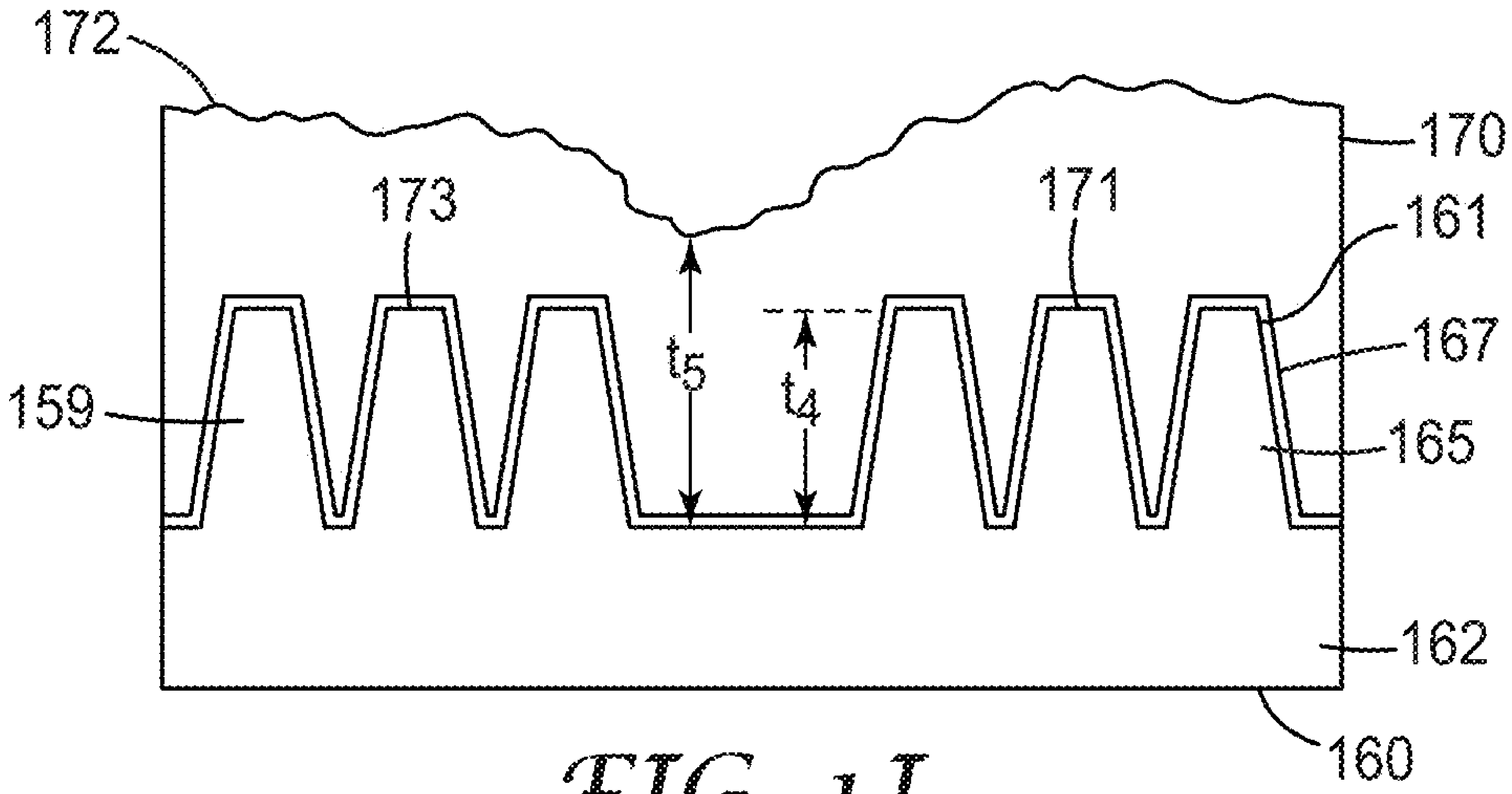


FIG. 1I



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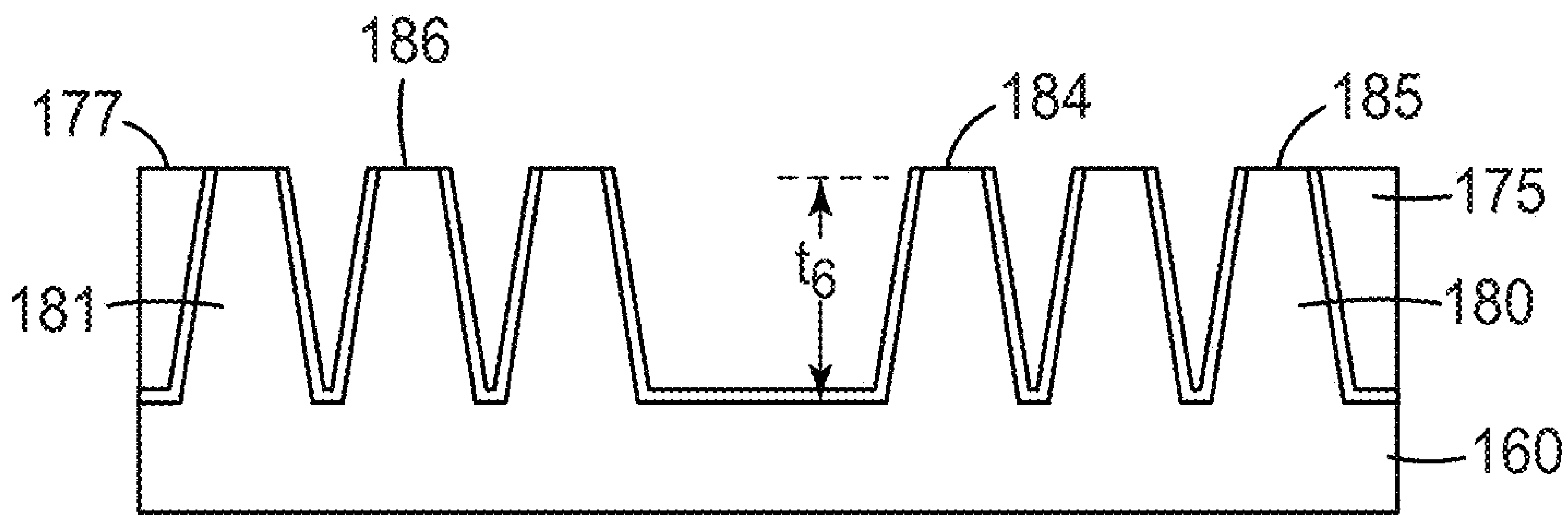

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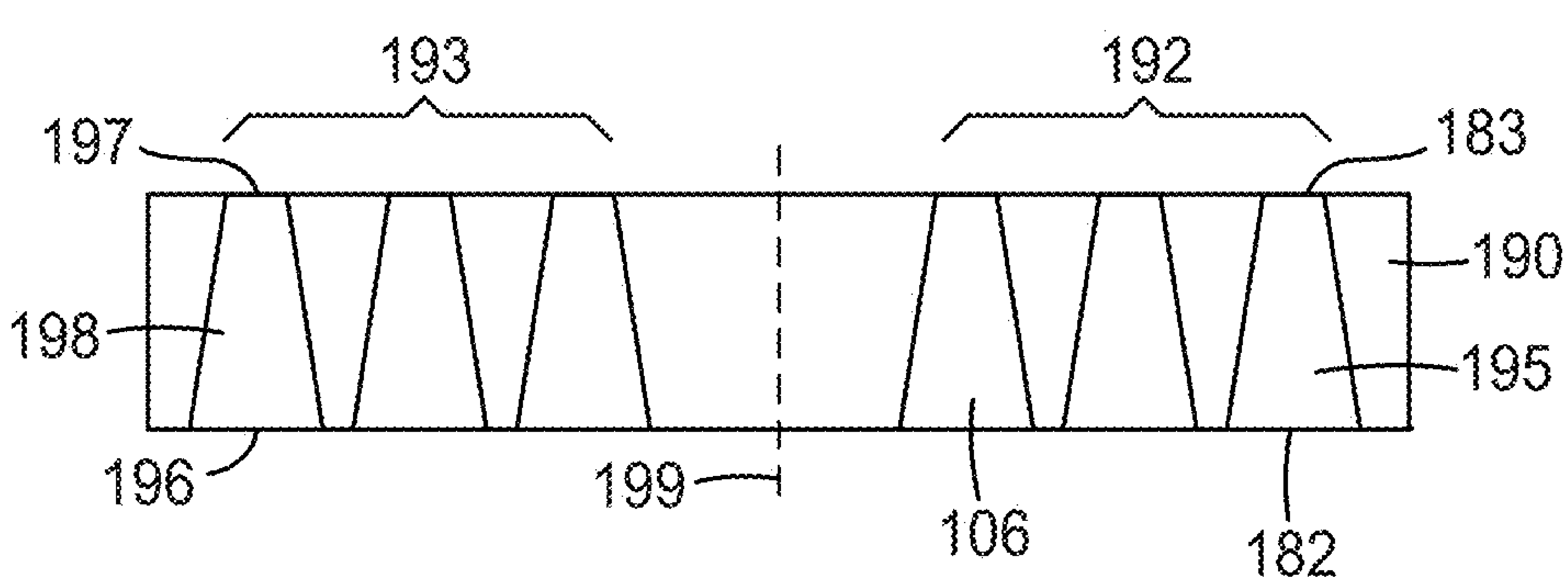

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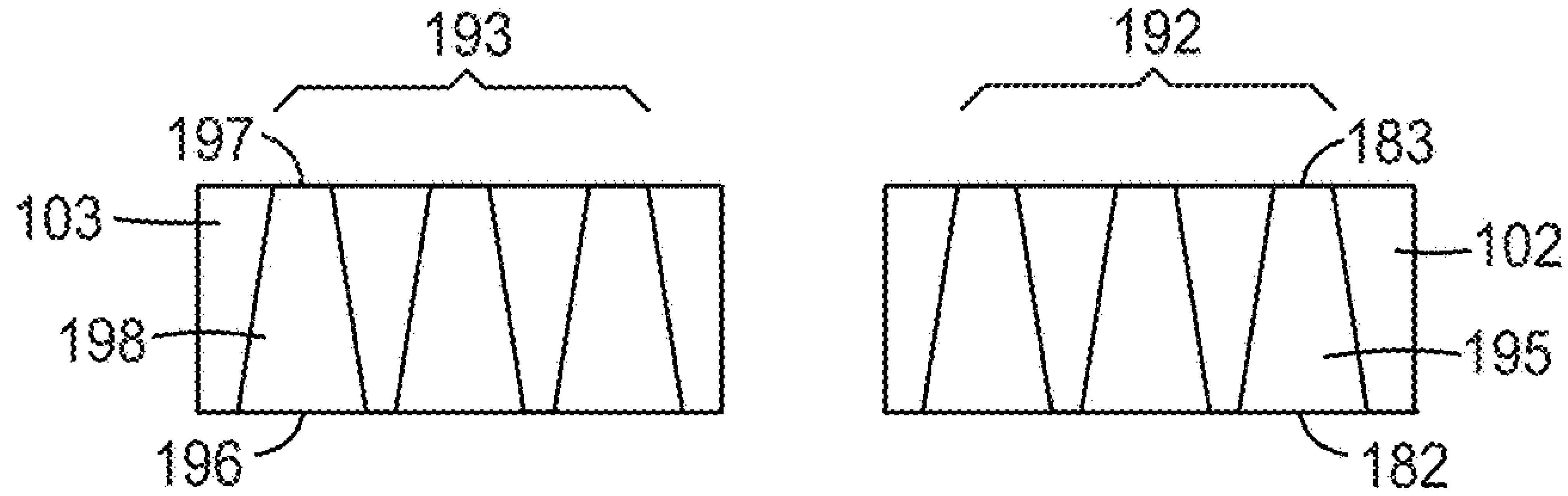

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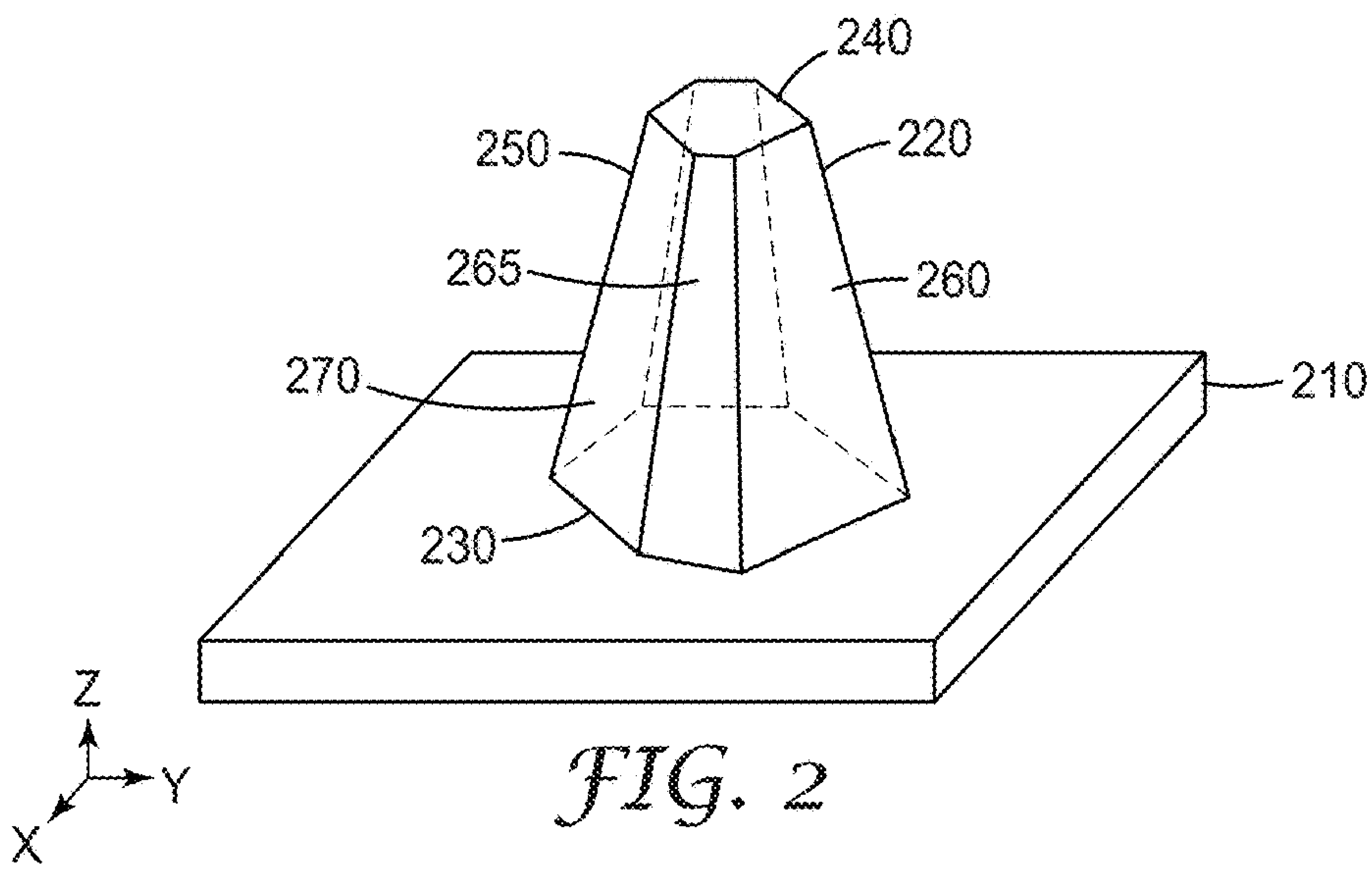

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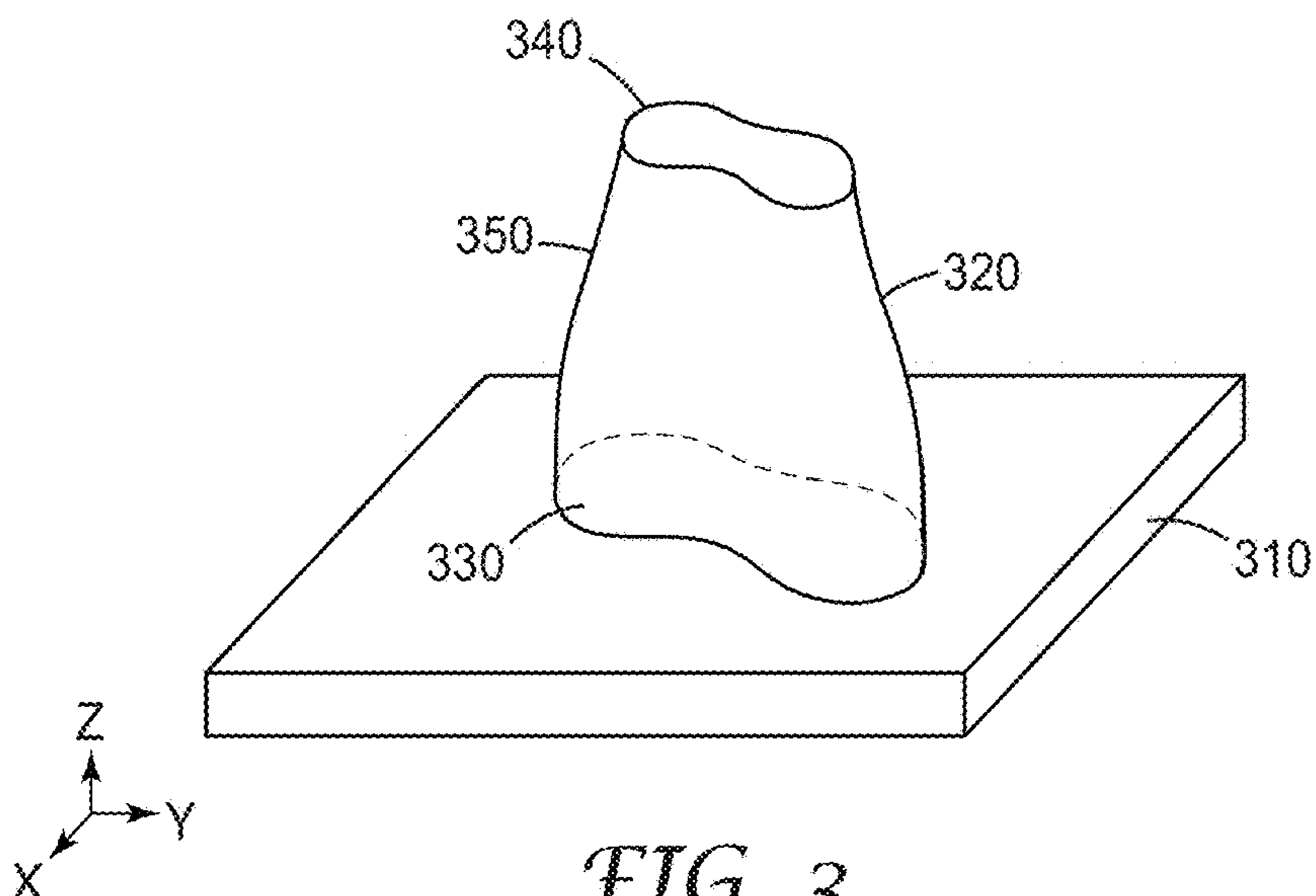

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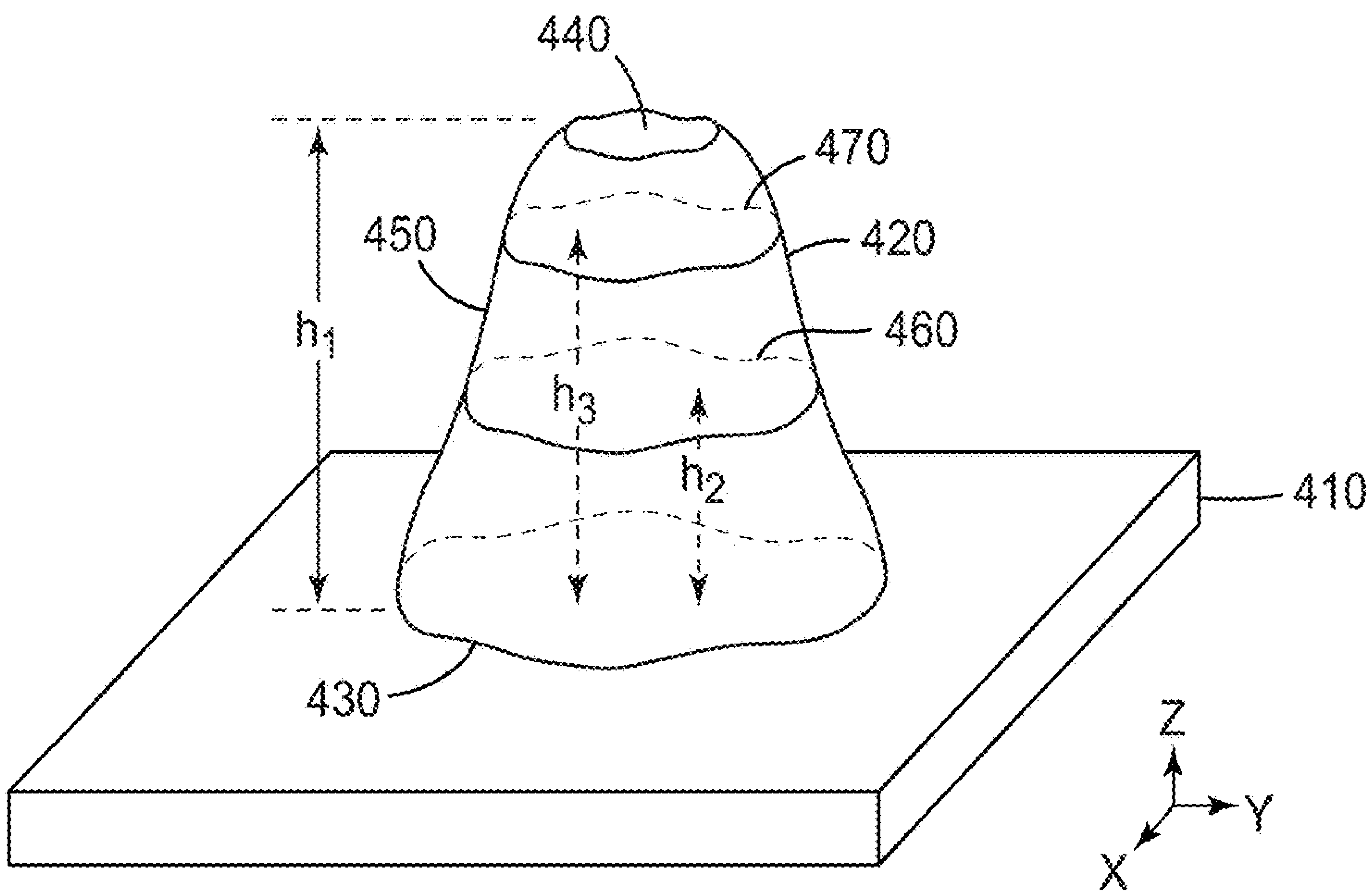

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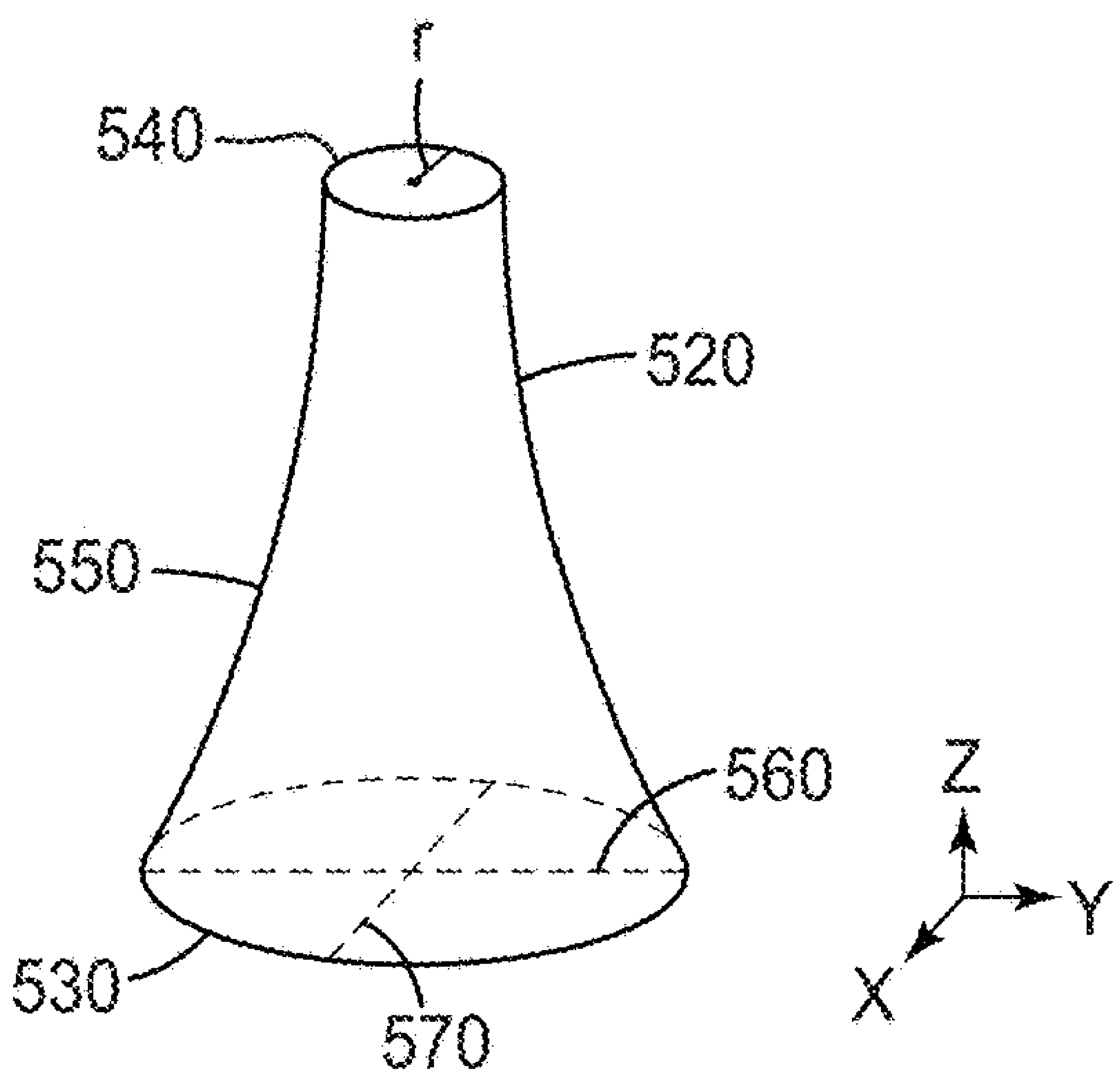

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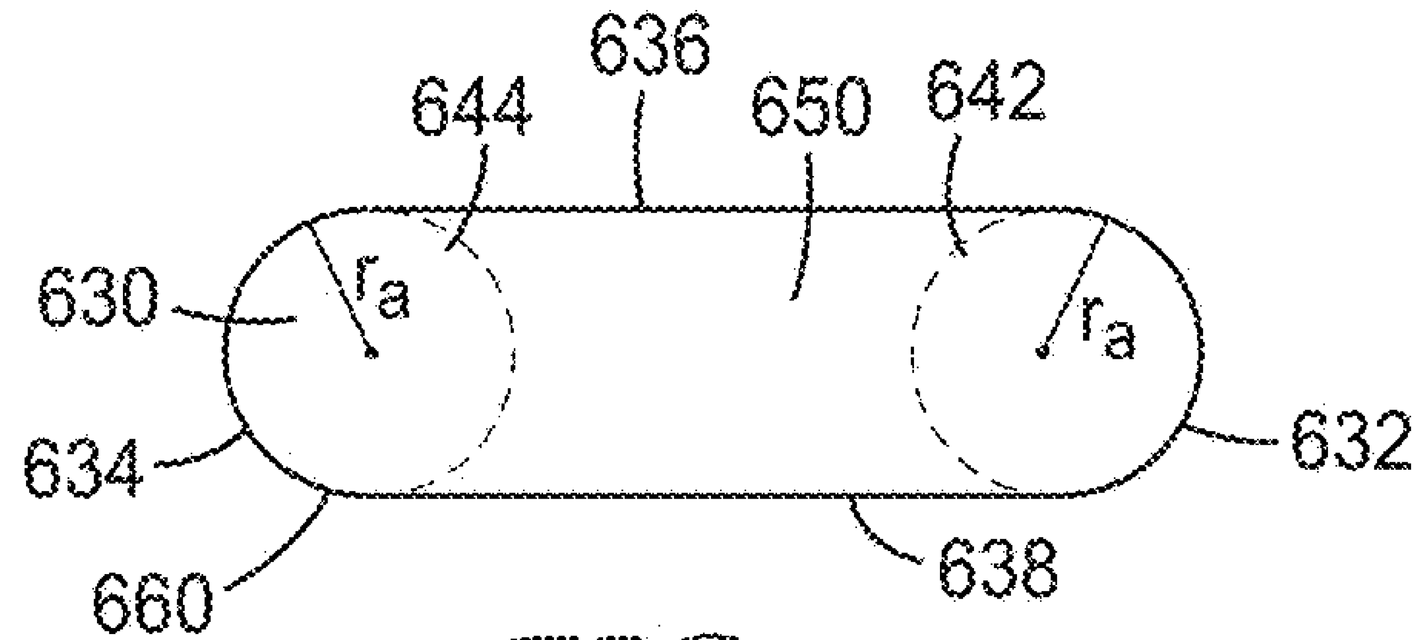

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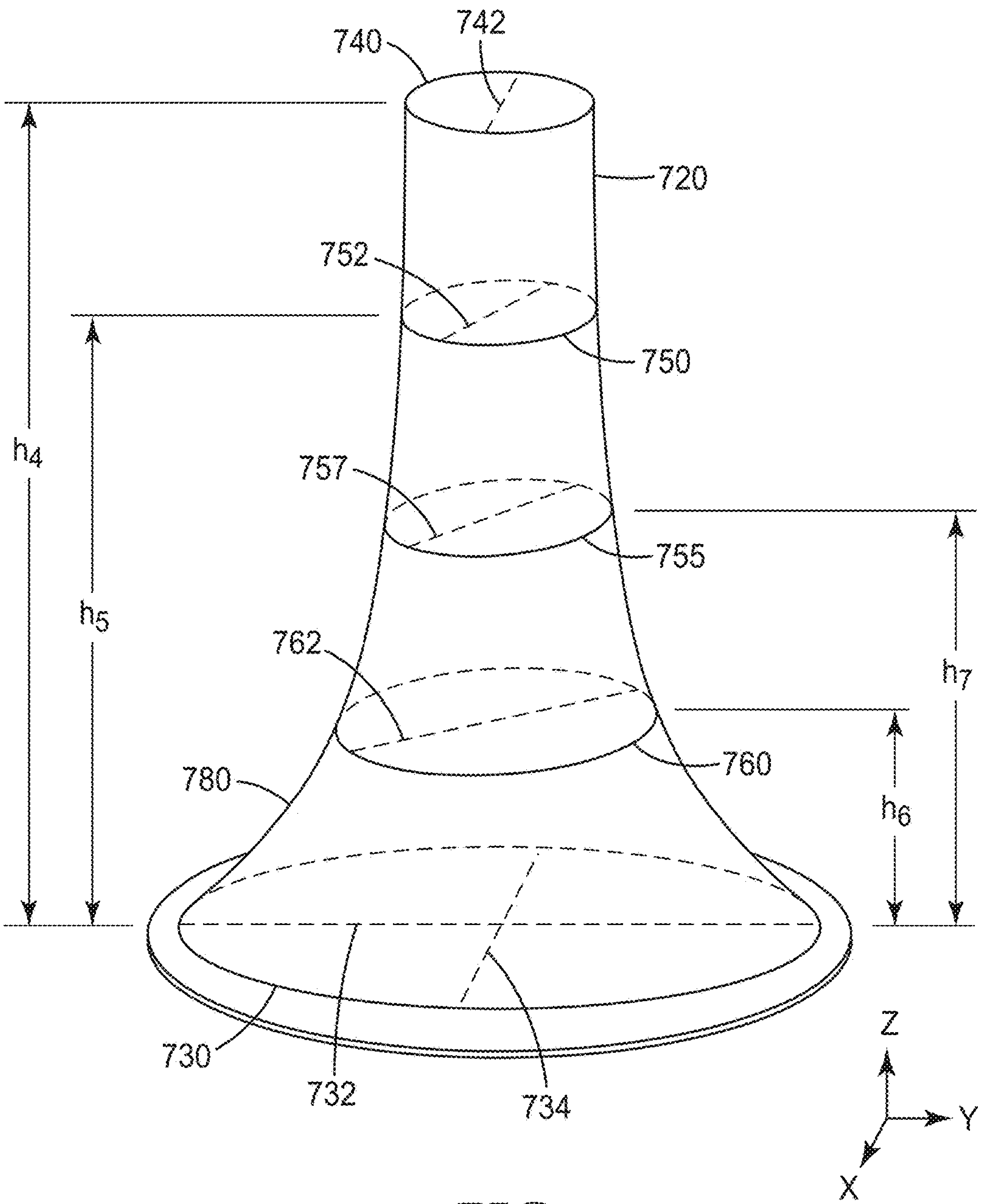
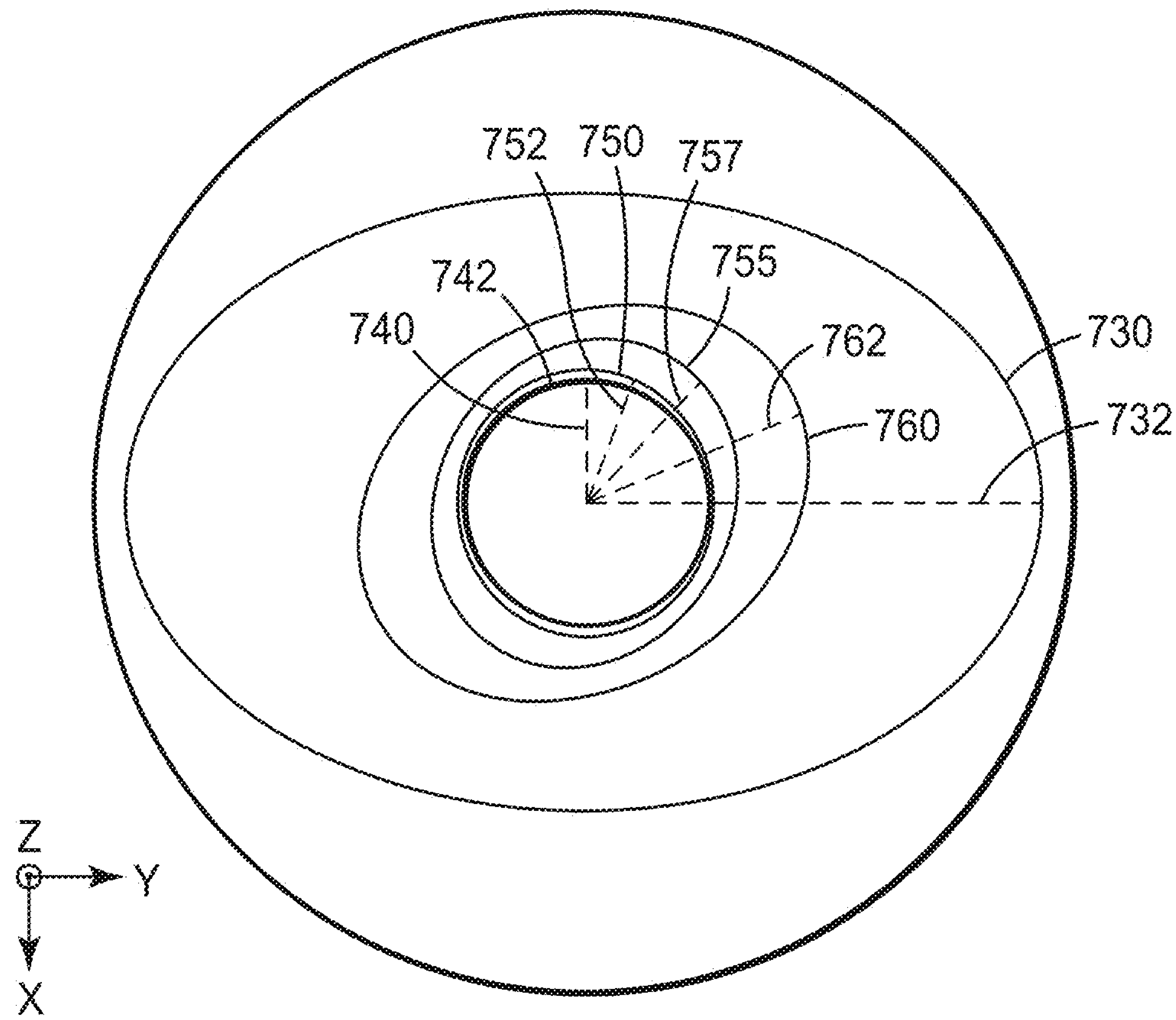


740
742
720
752
750
757
755
762
760
780
730
732
734
h4
h5
h6
h7
Z
Y
X

FIG. 7



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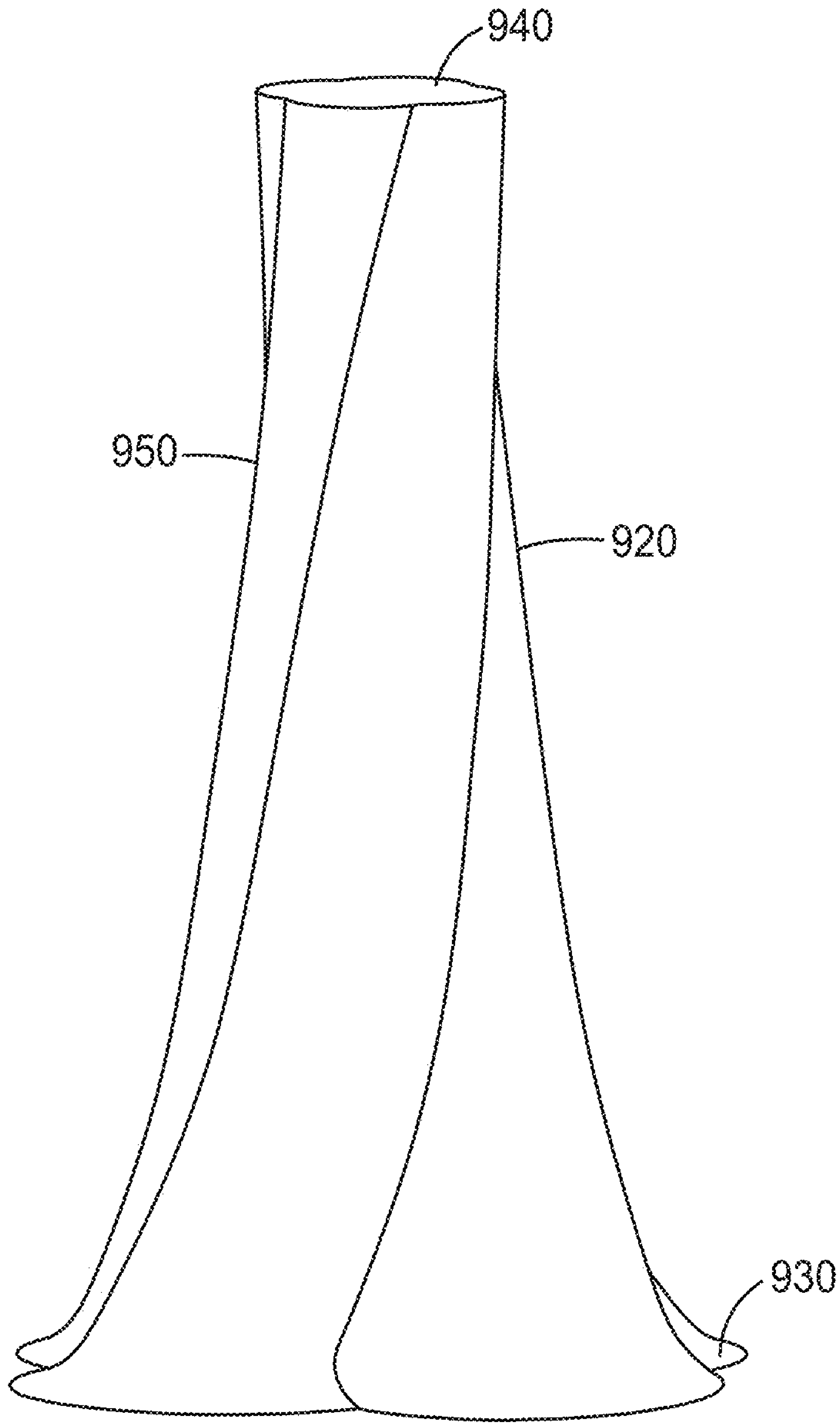
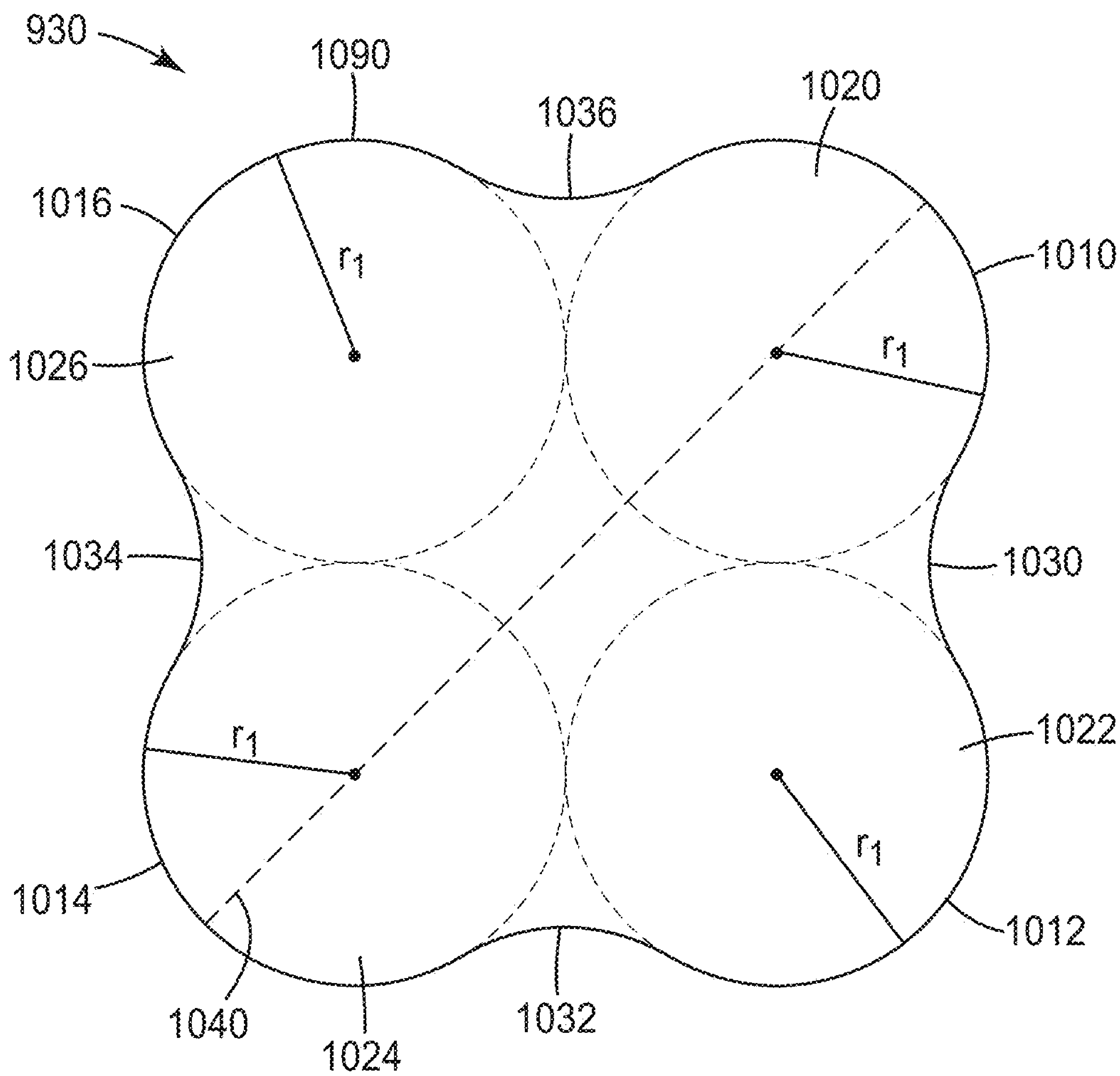


FIG. 9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1090
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1020
1016
1010
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1022
1014
1012
1040
1024
1032
r1
r1
r1
r1

FIG. 10

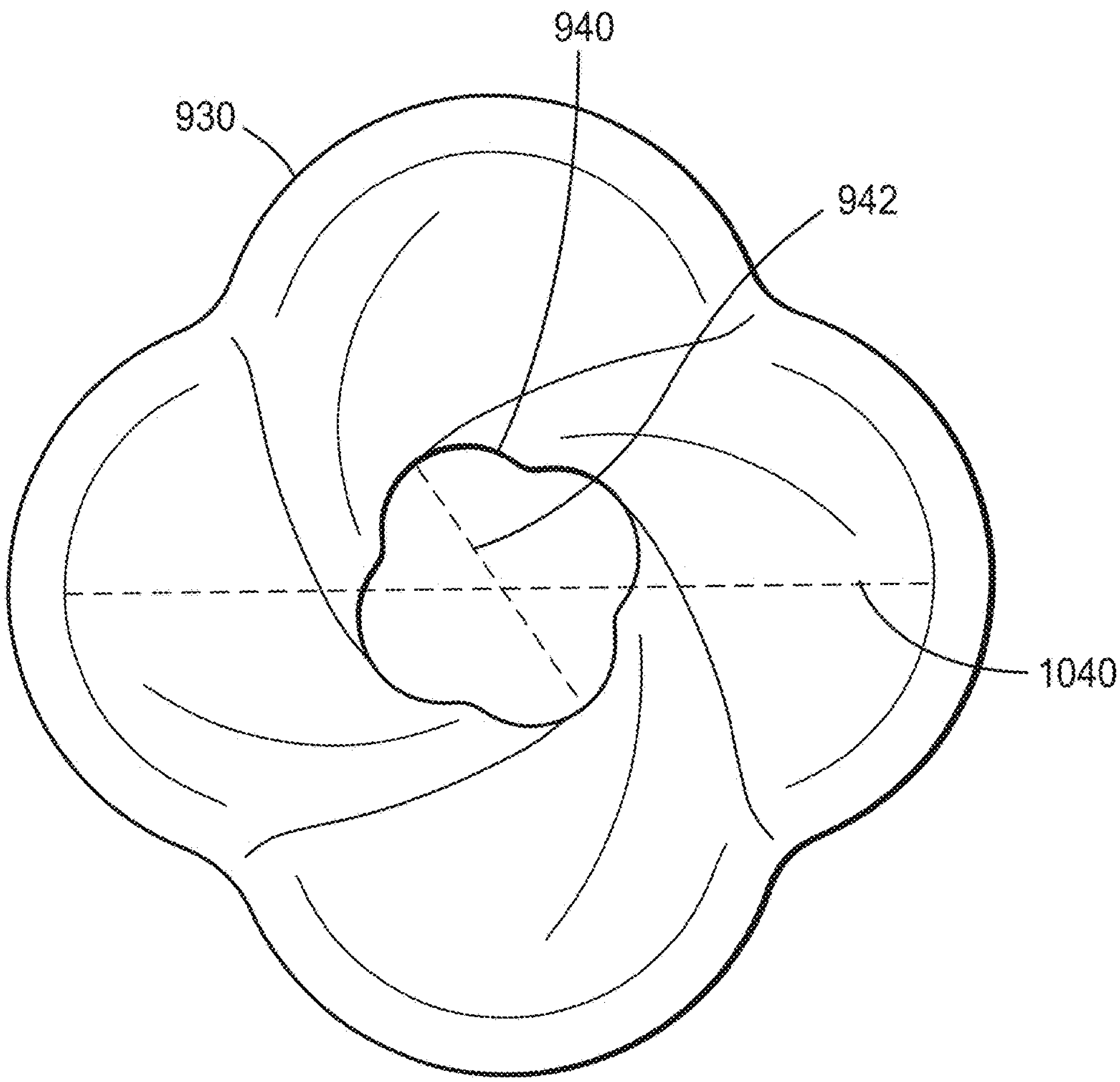
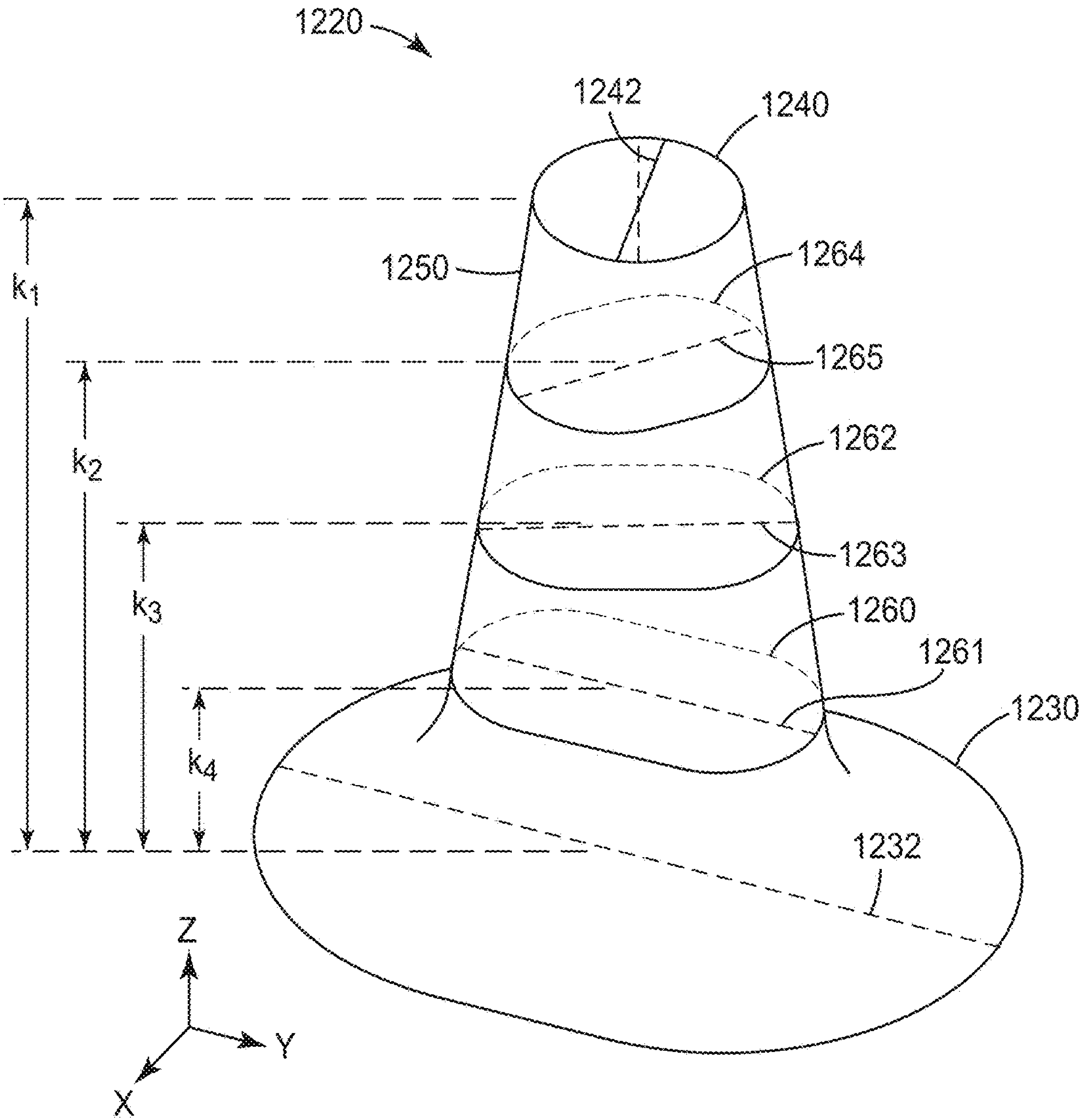


FIG. 11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1242
1240
1250
1264
1265
1262
1263
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1261
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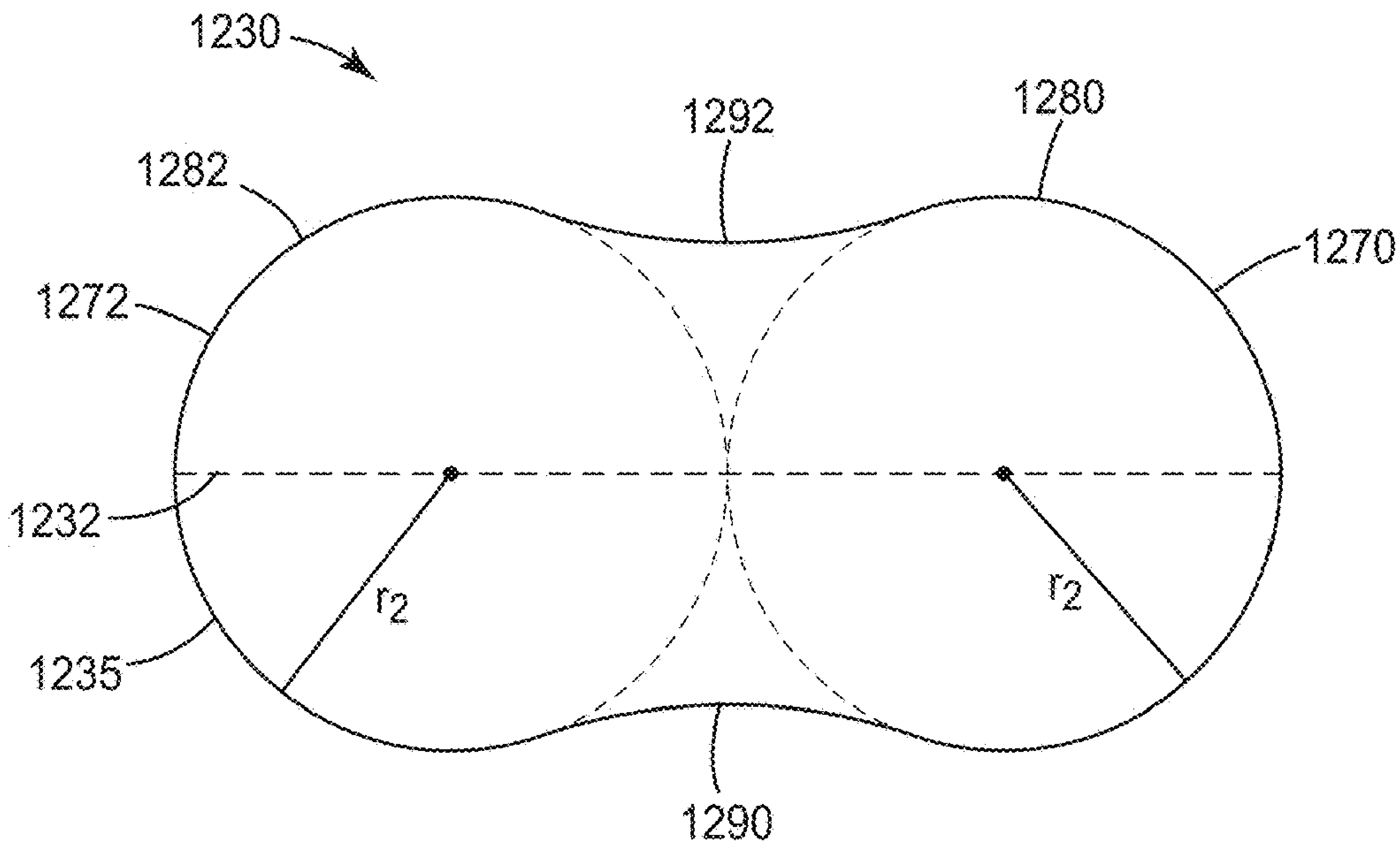
1232
k_1
k_2
k_3
k_4
Z
Y
X

FIG. 12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1272
1232
r_2
r_2
1235
1290

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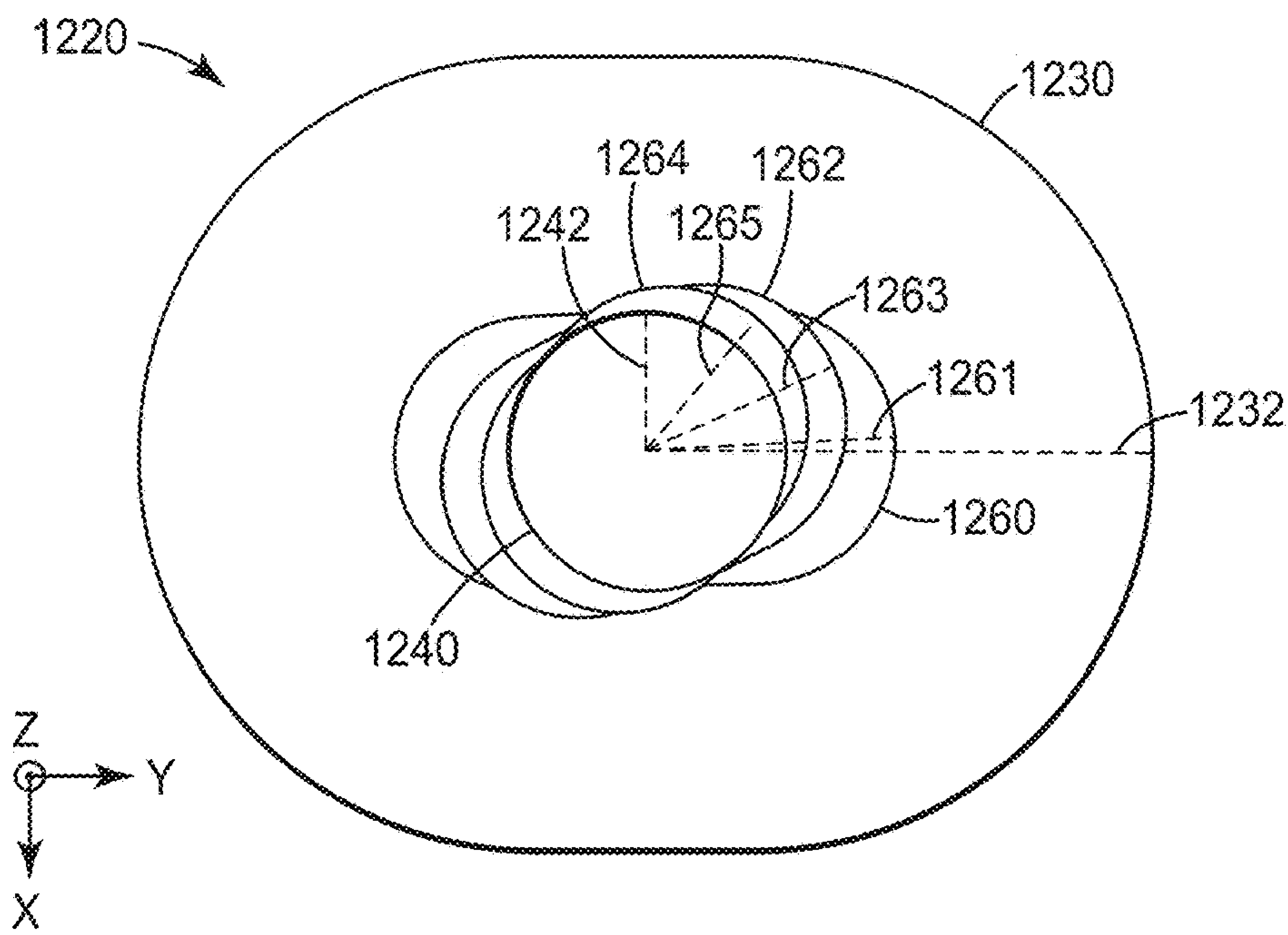
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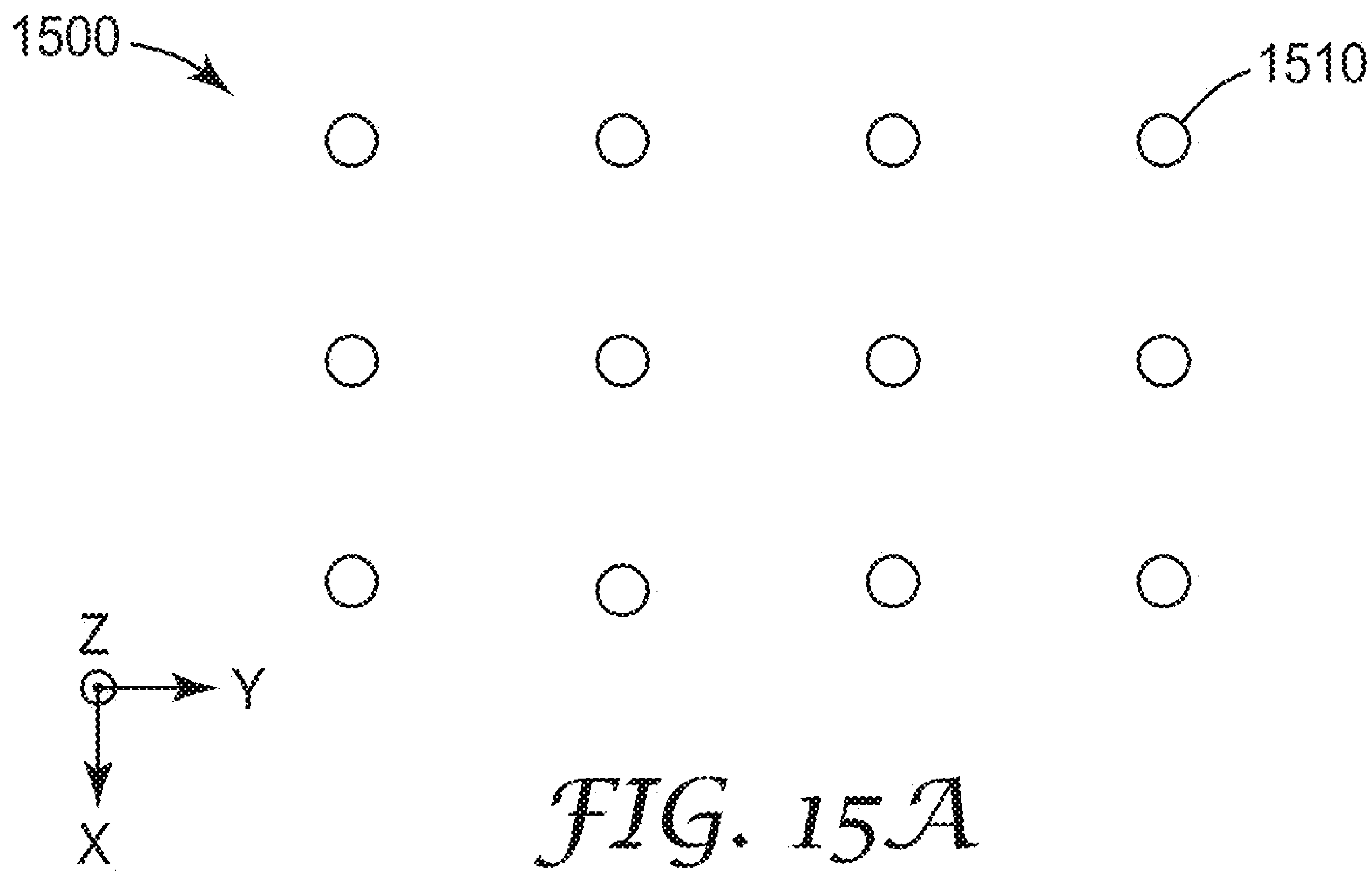
1260
1240
Z
Y
X

FIG. 14



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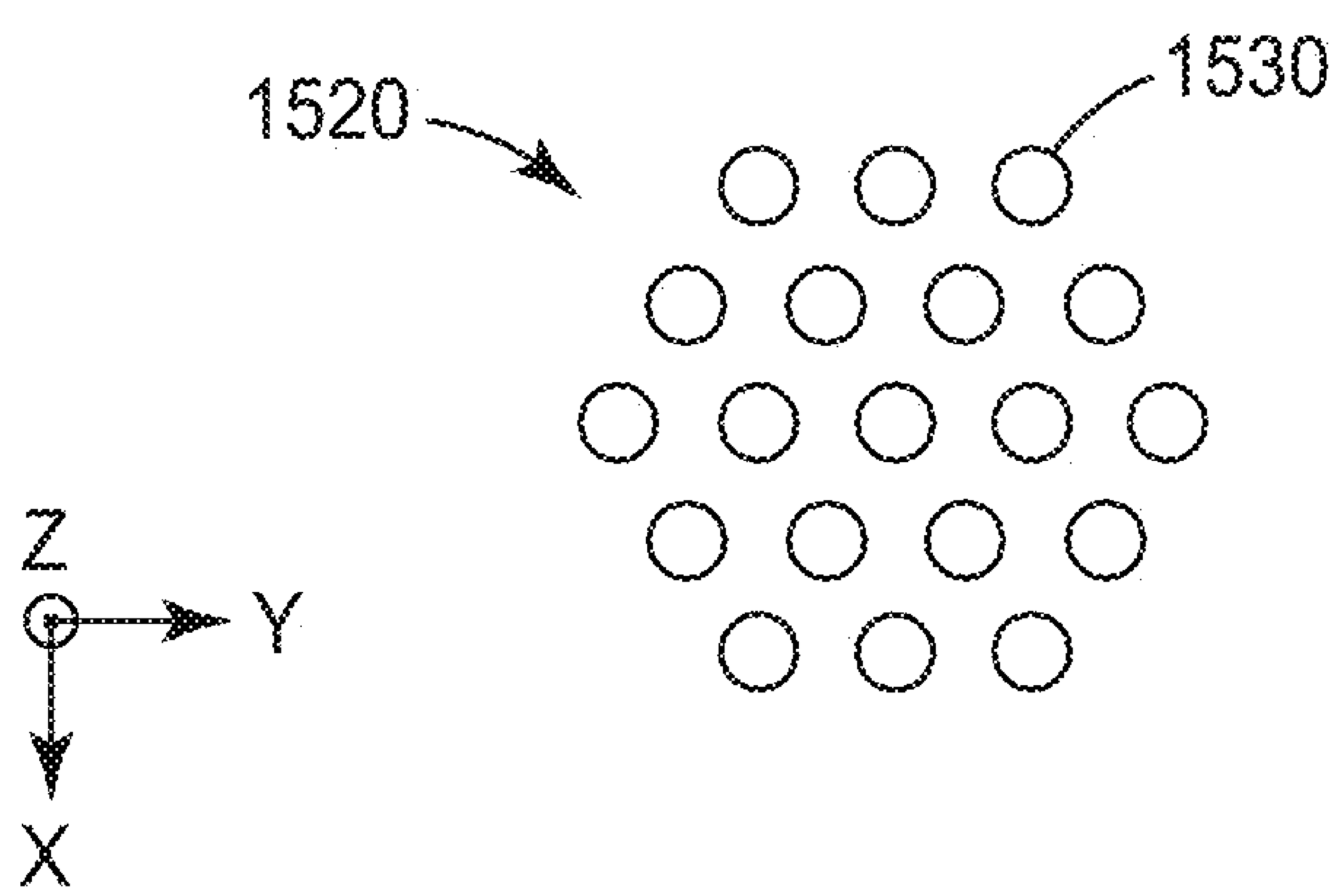
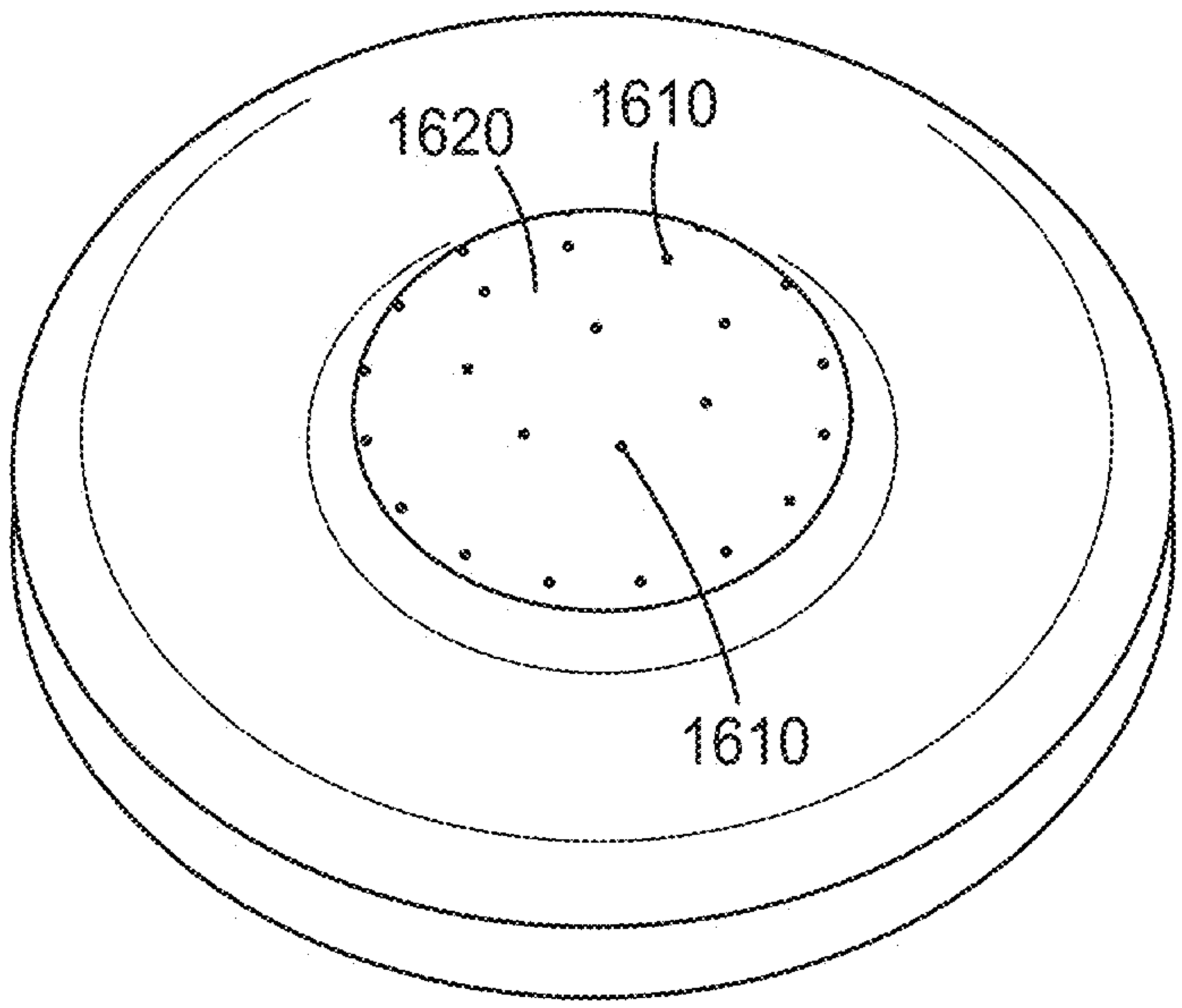


FIG. 15B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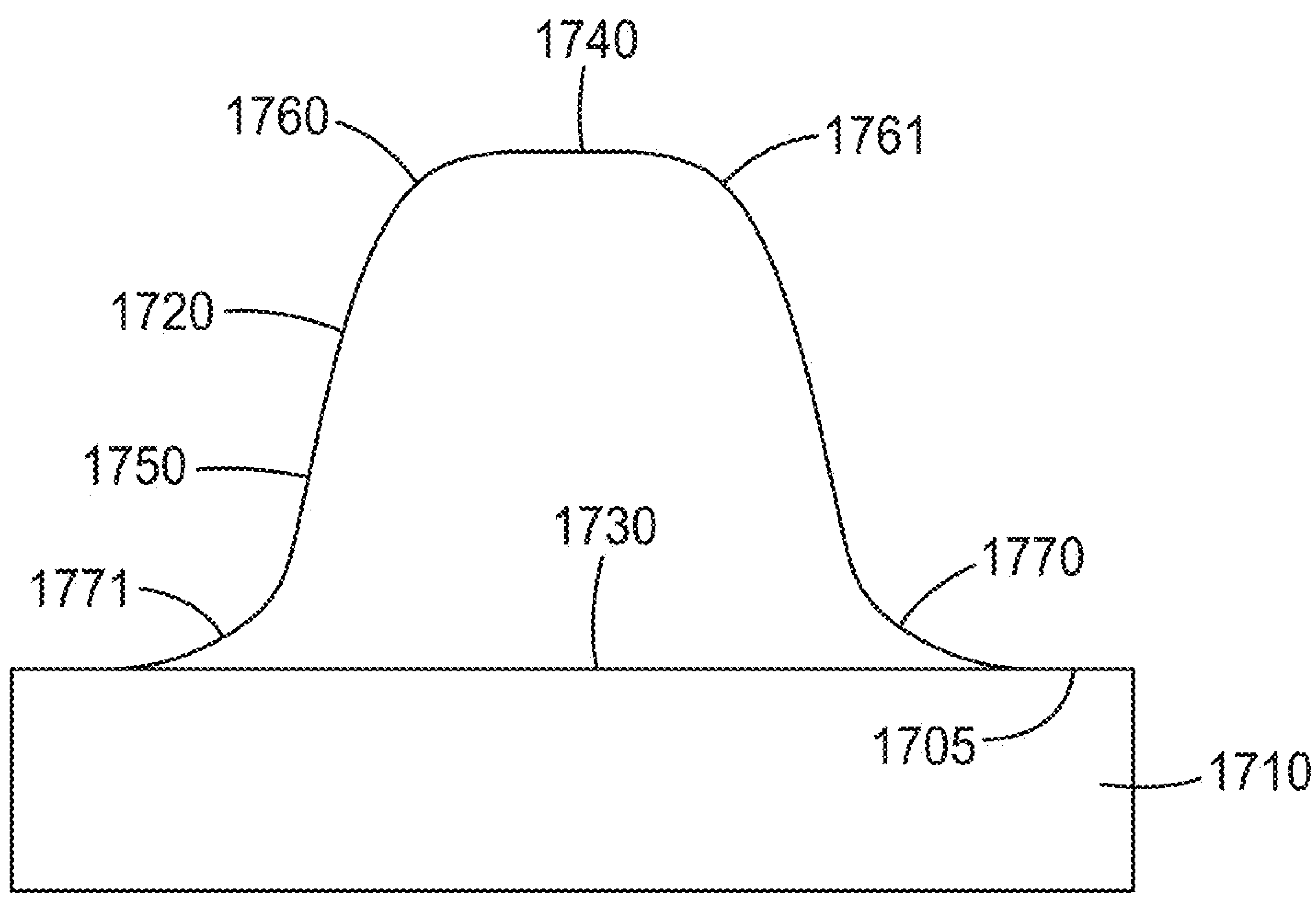
1610

FIG. 16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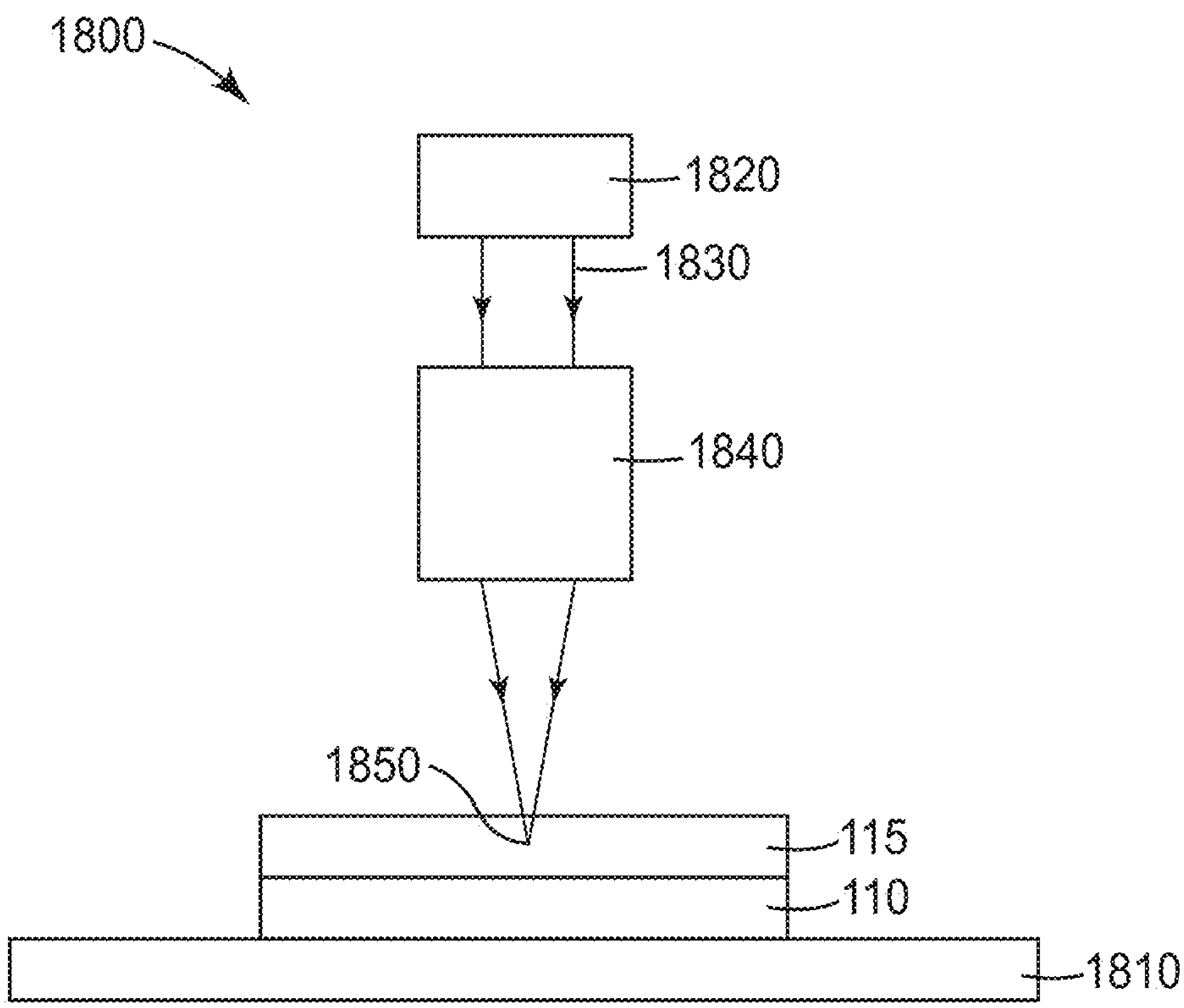
1710

FIG. 17



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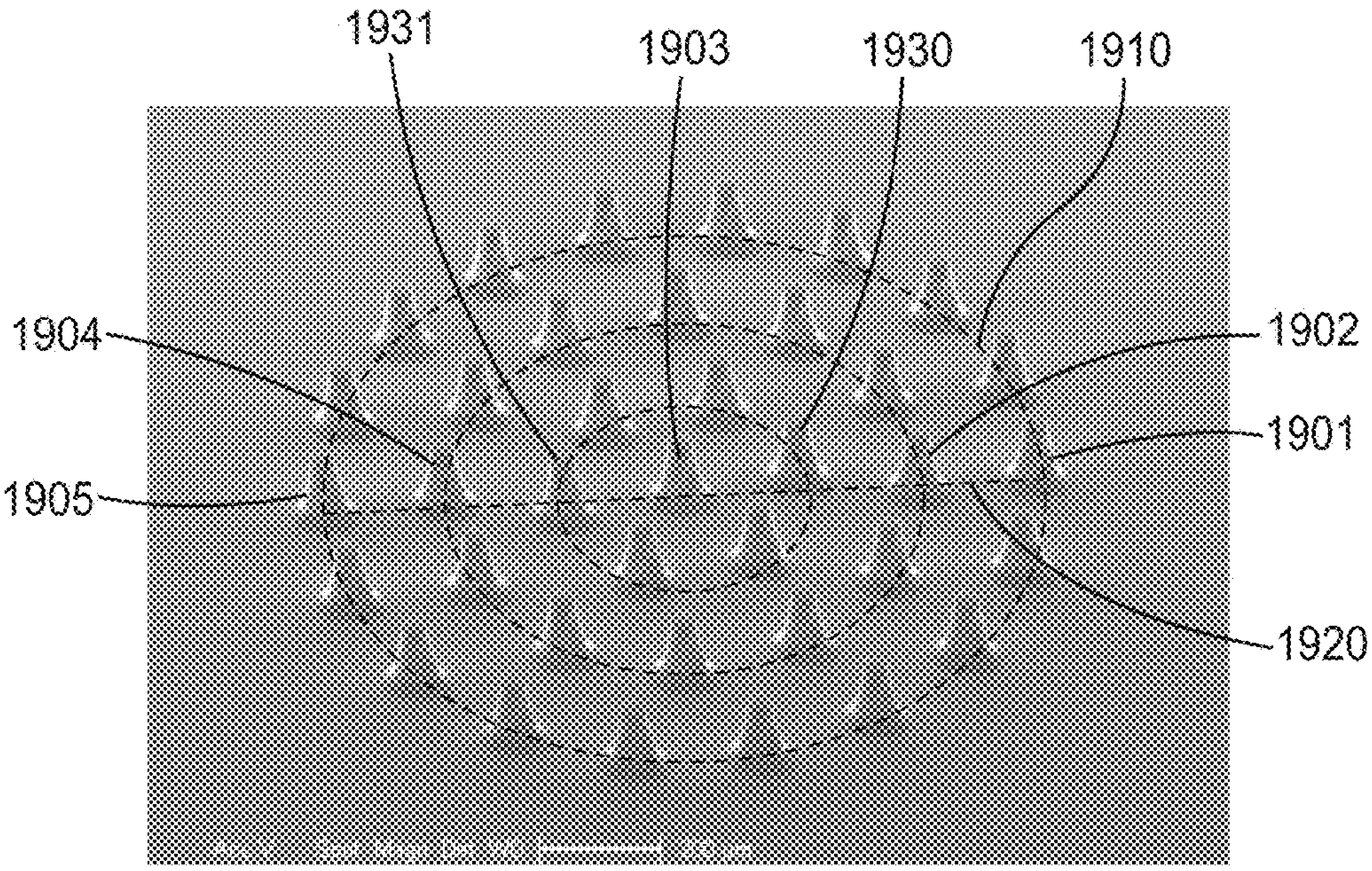

FIG. 19

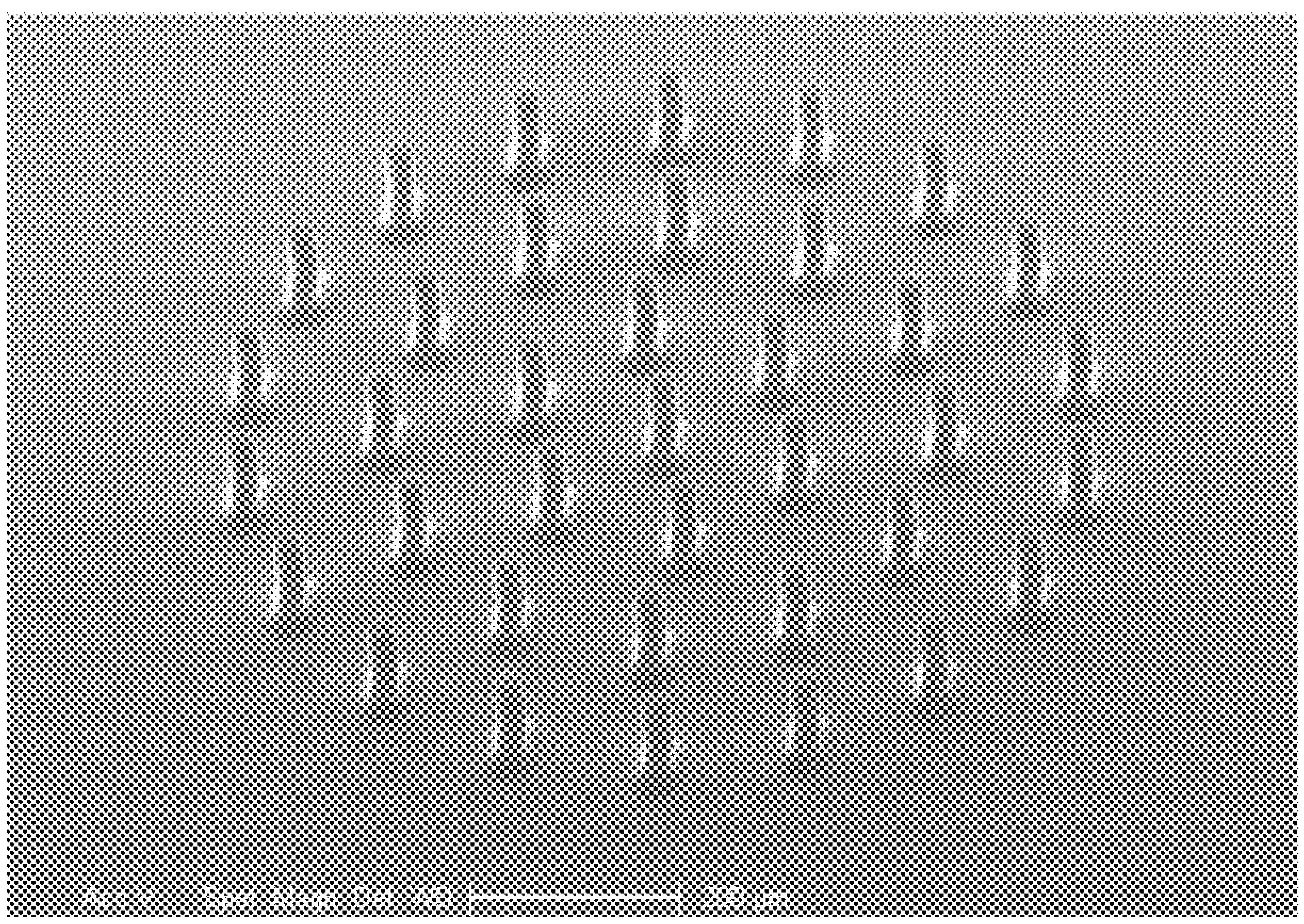

FIG. 20

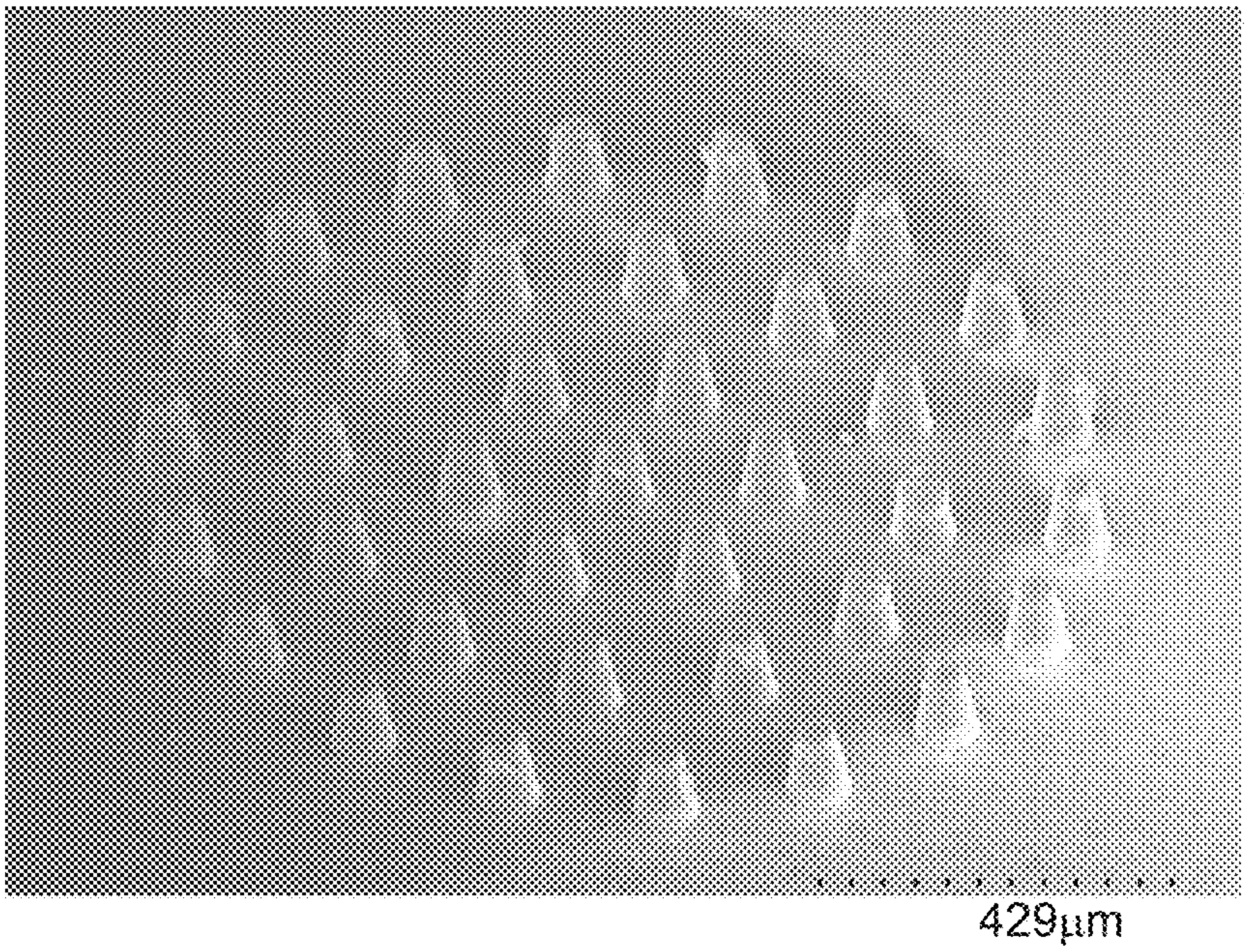

FIG. 21

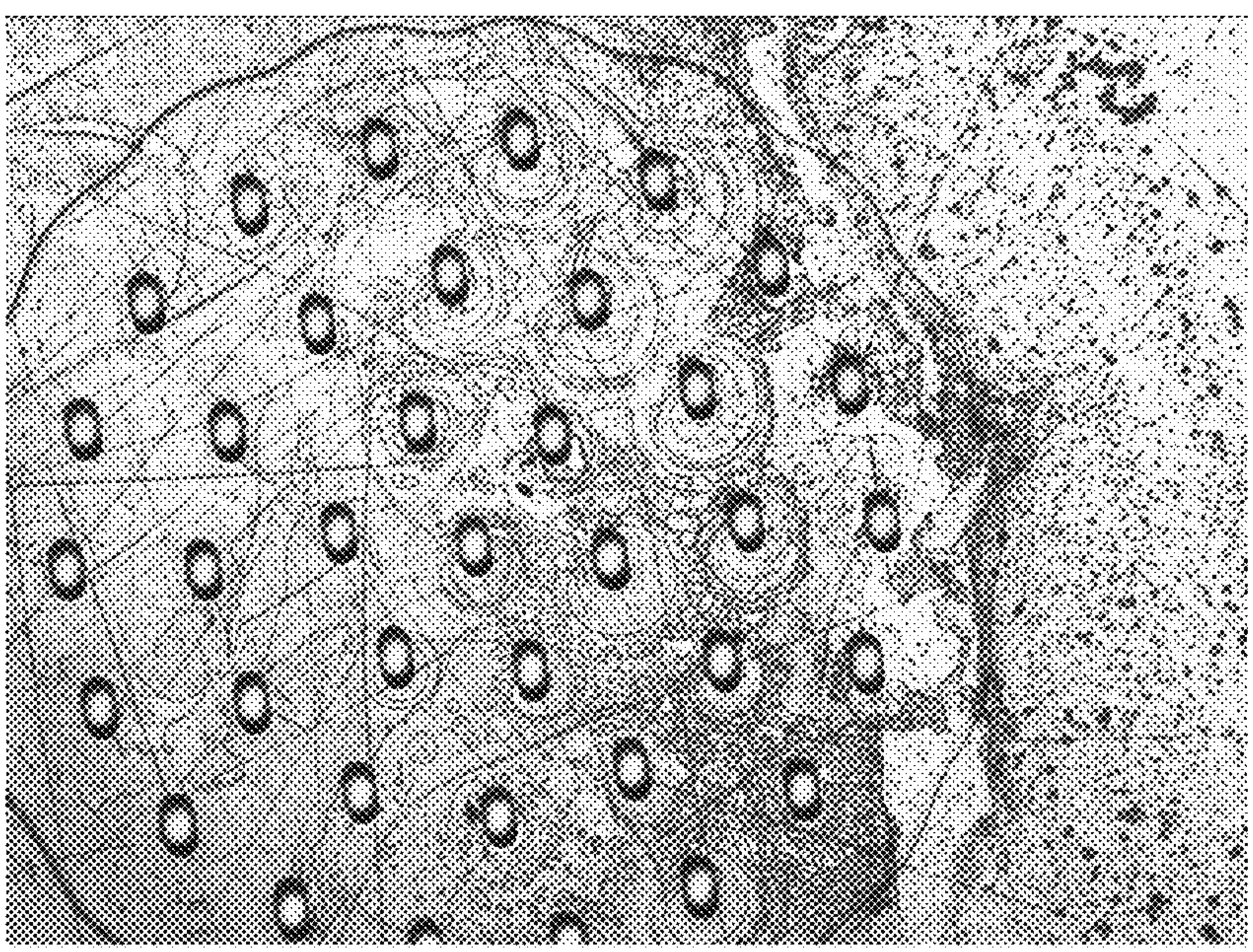

FIG. 22

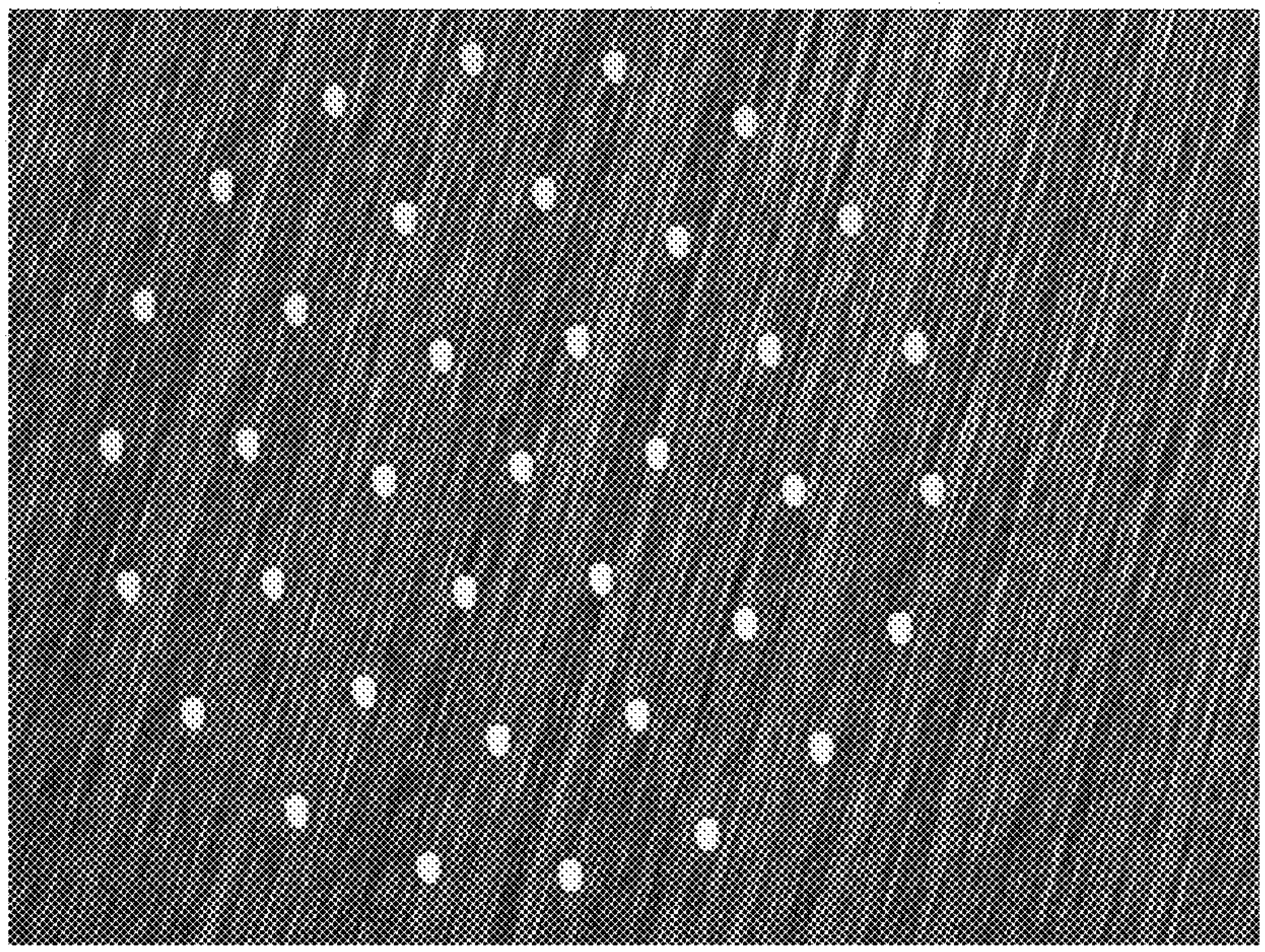

FIG. 23

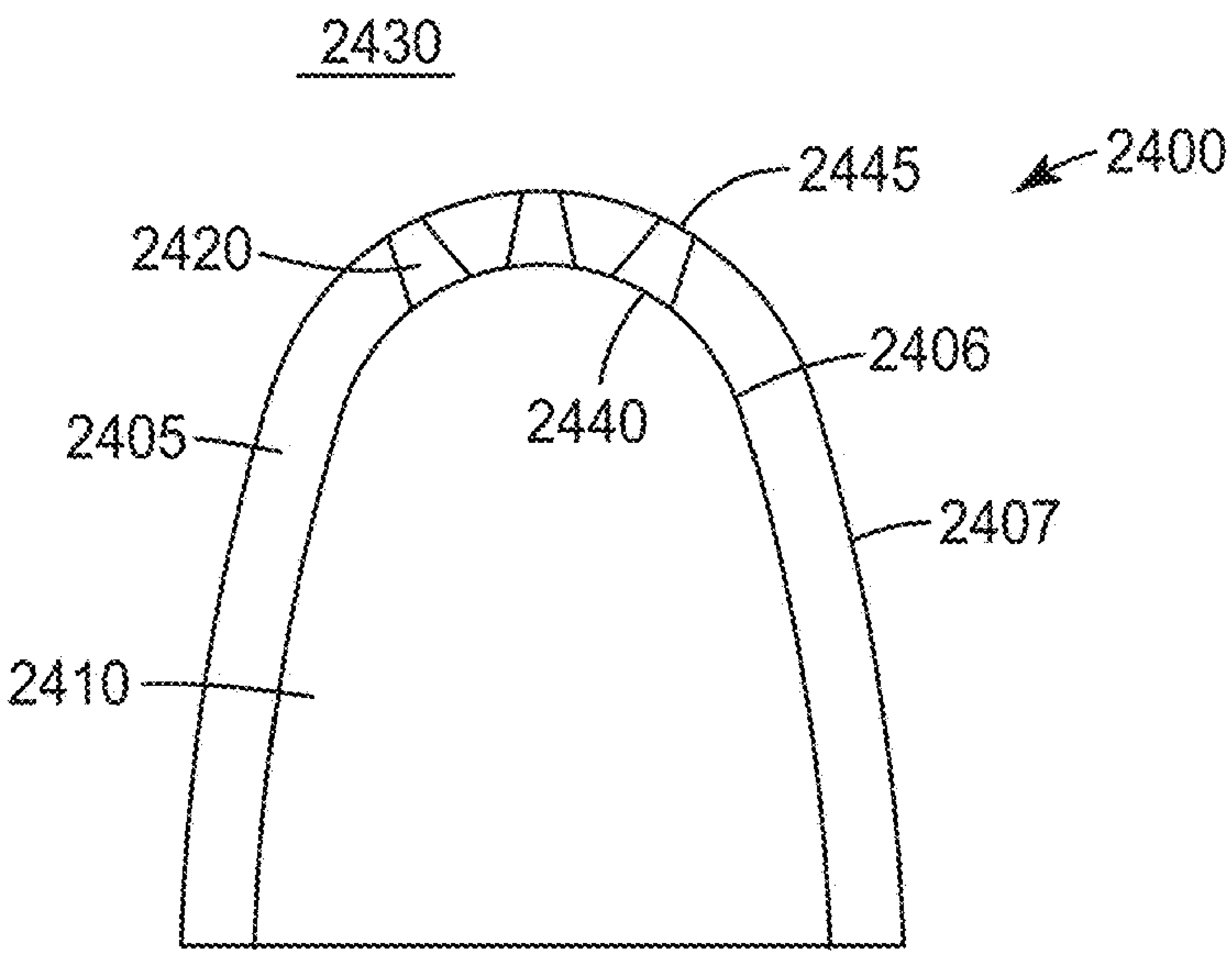

FIG. 24

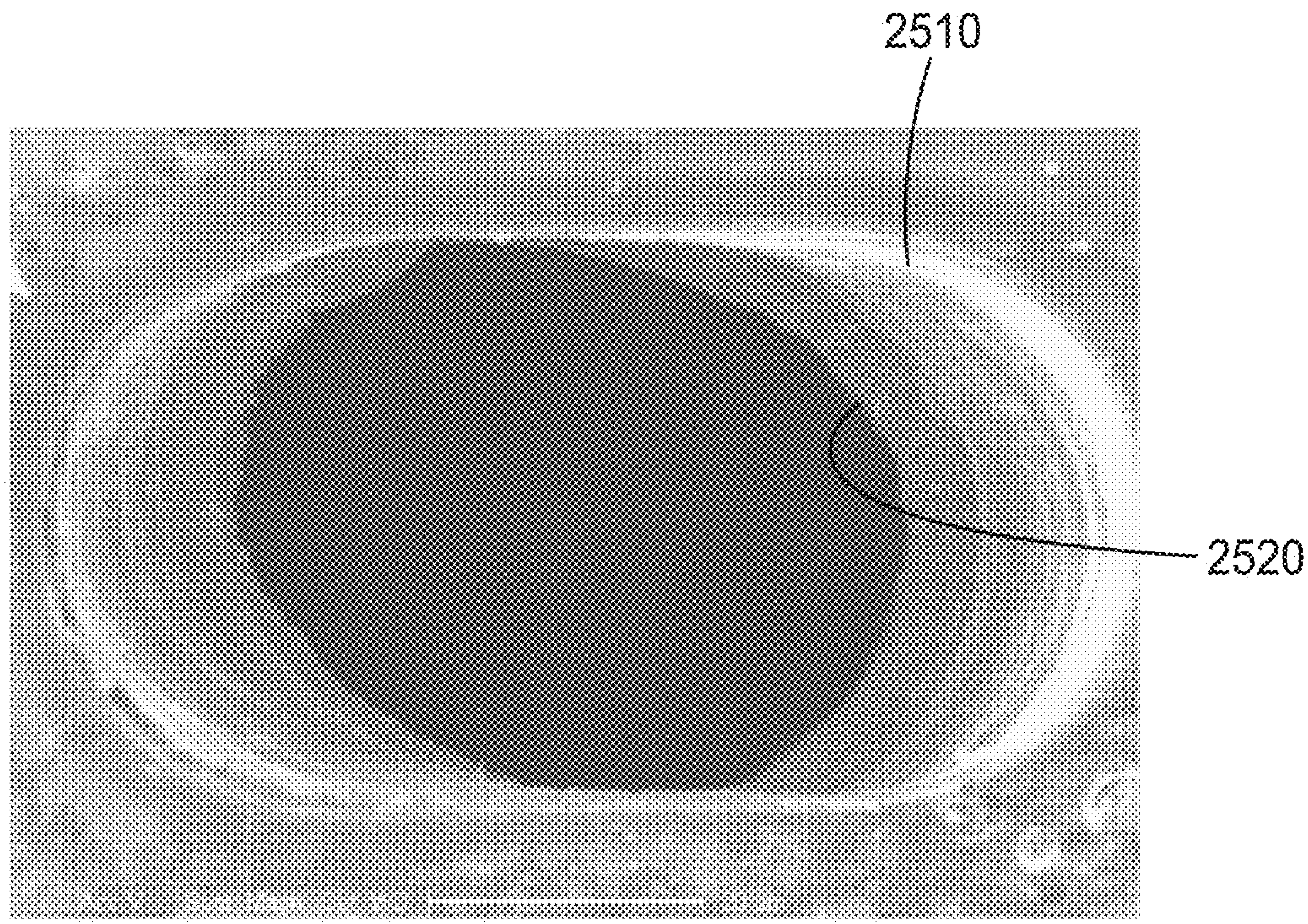

FIG. 25

FUEL INJECTOR NOZZLE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 13/387,550, filed Jan. 27, 2012, which is a 371 of International Application No. PCT/US2010/043628, filed Jul. 29, 2010, which claims benefit of provisional 61/229,821, filed Jul. 30, 2009, the disclosures of which are incorporated by reference in their entireties herein.

FIELD OF THE INVENTION

This invention generally relates to nozzles. The invention is further applicable to fuel injectors incorporating such nozzles.

BACKGROUND

Fuel injection is increasingly becoming the preferred method for mixing fuel and air in internal combustion engines. Fuel injection generally can be used to increase fuel efficiency of the engine and reduces hazardous emissions. Fuel injectors generally include a nozzle for atomizing the fuel under pressure for combustion. Increasing stringent environmental standards require more efficient fuel injectors.

SUMMARY OF THE INVENTION

Generally, the present invention relates to nozzles and methods of making nozzles. In one embodiment, a method of fabricating a nozzle includes the steps of: (a) providing a first material that is capable of undergoing multiphoton reaction; (b) forming a first microstructured pattern in the first material using a multiphoton process; (c) replicating the first microstructured pattern in a second material different than the first material to make a first mold that includes a second microstructured pattern in the second material; (d) replicating the second microstructured pattern in a third material that is different than the first and second materials to make a second mold that includes a third microstructured pattern that includes a plurality of microstructures in the third material; (e) planarizing the third microstructured pattern of the second mold with a layer of a fourth material that is different than the third material, where the layer exposes the tops of the microstructures in the plurality of microstructures in the third microstructured pattern; and (f) removing the third material resulting in a nozzle that has a plurality of holes in the fourth material, where the holes correspond to the plurality of microstructures in the third microstructured pattern. In some cases, the steps in the method are carried sequentially. In some cases, the first material includes poly(methyl methacrylate). In some cases, the first material is capable of undergoing a two photon reaction. In some cases, the first microstructured pattern includes a plurality of discrete microstructures. In some cases, the plurality of discrete microstructures includes a discrete microstructure that is a three-dimensional rectilinear body, a portion of a three-dimensional rectilinear body, a three-dimensional curvilinear body, a portion of a three-dimensional curvilinear body, a polyhedron, a cone, a tapered microstructure, or a spiraling microstructure. In some cases, the first microstructured pattern is formed in the first material using a two photon process. In some cases, the step of forming the first microstructured pattern in the first

material includes exposing at least a portion of the first material to cause a simultaneous absorption of multiple photons. In some cases, the step of forming the first microstructured pattern in the first material includes removing the exposed portions of the first material, or the unexposed portions of the first material. In some cases, replicating the first microstructured pattern in the second material includes electroplating the first microstructured pattern. In some cases, the second material comprises an electroplating material. In some cases, the first mold comprises a metal. In some cases, the first mold comprises Ni. In some cases, the second microstructured pattern is substantially a negative replica of the first microstructured pattern. In some cases, the step of replicating the second microstructured pattern in the third material includes injection molding. In some cases, the third material includes a polymer, such as polycarbonate. In some cases, the second mold includes a polymer. In some cases, the third microstructured pattern is substantially a negative replica of the second microstructured pattern. In some cases, the step of planarizing the third microstructured pattern includes electroplating the third microstructured pattern. In some cases, the step of planarizing the third microstructured pattern includes coating the third microstructured pattern with the fourth material. In some cases, the step of planarizing the third microstructured pattern includes electroplating the third microstructured pattern with the fourth material. In some cases, the step of planarizing the third microstructured pattern includes removing a portion of the fourth material, where, in some cases, the portion of the coated fourth material is removed by a grinding method. In some cases, the fourth material includes an electroplating material. In some cases, the nozzle includes a metal. In some cases, the nozzle includes Ni.

In another embodiment, a nozzle includes a hollow interior and at least one hole that connects the hollow interior with an outside of the nozzle. The at least one hole includes a hole entry at the hollow interior of the nozzle having a first shape, and a hole exit at the outside of the nozzle having a second shape that is different than the first shape. In some cases, the first shape is an elliptical shape and the second shape is a circular shape. In some cases, the first shape is a racetrack shape and the second shape is a circular shape. In some cases, the perimeter of the first shape includes the outer arcs of a plurality of closely packed circles, where the outer arcs are connected by curve-like fillets.

In another embodiment, a nozzle includes a hollow interior and at least one hole that connects the hollow interior with an outside of the nozzle. The at least one hole includes a hole entry at the hollow interior of the nozzle and a hole exit at the outside of the nozzle. The at least one hole has a cross-section that rotates from the hole entry to the hole exit. In some cases, the cross-section has an increasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section has a decreasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section has a constant rotation rate from the hole entry to the hole exit. In some cases, the hole entry has a first shape and the hole exit has a second shape that is different than the first shape. In some cases, the nozzle includes a plurality of holes that are arranged in an array of concentric circles that includes an outermost circle. The discrete nozzle holes are arranged such that no diameter of the outermost circle includes at lease one discrete nozzle hole from each circle in the array of concentric circles. In some cases, each circle in the array of concentric circles includes equally spaced discrete nozzle holes.

BRIEF DESCRIPTION OF DRAWINGS

The invention may be more completely understood and appreciated in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIGS. **1A-1M** are schematic representations of constructions at intermediate stages or steps in a process for fabricating a nozzle;

FIG. **2** is a schematic three-dimensional view of a microstructure;

FIG. **3** is a schematic three-dimensional view of another microstructure;

FIG. **4** is a schematic three-dimensional view of another microstructure;

FIG. **5** is a schematic three-dimensional view of another microstructure;

FIG. **6** is a schematic of a base of a microstructure;

FIGS. **7** and **8** are respective schematic three-dimensional and top views of a microstructure;

FIG. **9** is a schematic three-dimensional view of a microstructure (nozzle hole);

FIG. **10** is a schematic of the base (hole entry) of the microstructure (nozzle hole) shown in FIG. **9**;

FIG. **11** is a schematic top-view of the microstructure (nozzle hole) shown in FIG. **9**;

FIG. **12** is a schematic three-dimensional view of a nozzle hole (microstructure);

FIG. **13** is a schematic of the hole entry (base) of the nozzle hole (microstructure) shown in FIG. **12**;

FIG. **14** is a schematic top-view of the nozzle hole (microstructure) shown in FIG. **12**;

FIGS. **15**A and B are schematic top-views of two different arrays of holes (microstructures);

FIG. **16** is a schematic three-dimensional view of a plurality of nozzle holes (microstructures);

FIG. **17** is a schematic side-view of a microstructure;

FIG. **18** is a schematic side-view of an exposure system;

FIGS. **19** and **20** are two scanning electron micrographs (SEM) of a cluster of microstructures;

FIG. **21** is an SEM of a cluster of polycarbonate microstructures;

FIGS. **22** and **23** are optical micrographs of respective hole entries and hole entries of a cluster of holes;

FIG. **24** is a schematic side-view of a nozzle; and

FIG. **25** is an SEM of one of the holes shown in FIGS. **22** and **23**.

In the specification, a same reference numeral used in multiple figures refers to the same or similar elements having the same or similar properties and functionalities.

DETAILED DESCRIPTION

This invention generally relates to spray nozzles. The disclosed nozzles include one or more holes designed to improve spray direction and fluid dynamics at the hole inlet, within the hole wall, and at the hole outlet. The disclosed nozzles can advantageously be incorporated into fuel injector systems to improve fuel efficiency. The disclosed nozzles can be fabricated using multiphoton, such as two photon, processes. In particular, multiphoton processes can be used to fabricate microstructures that can, in turn, be used as molds to fabricate holes for use in nozzles or other applications.

It should be understood that the term "nozzle" may have a number of different meanings in the art. In some specific references, the term nozzle has a broad definition. For example, U.S. Patent Publication No. 2009/0308953 A1 (Palestrant et al.), discloses an "atomizing nozzle" which includes a number of elements, including an occluder chamber **50**. This differs from the understanding and definition of nozzle put forth herewith. For example, the nozzle of the current description would correspond generally to the orifice insert **24** of Palestrant et al. In general, the nozzle of the current description can be understood as the final tapered portion of an atomizing spray system from which the spray is ultimately emitted, see e.g., Merriam Webster's dictionary definition of nozzle ("a short tube with a taper or constriction used (as on a hose) to speed up or direct a flow of fluid." Further understanding may be gained by reference to U.S. Pat. No. 5,716,009 (Ogihara et al.) issued to Nippondenso Co., Ltd. (Kariya, Japan). In this reference, again, fluid injection "nozzle" is defined broadly as the multi-piece valve element **10** ("fuel injection valve **10** acting as fluid injection nozzle . . . "—see col. 4, lines 26-27 of Ogihara et al.). The current definition and understanding of the term "nozzle" as used herein would relate to first and second orifice plates **130** and **132** and potentially sleeve **138** (see FIGS. 14 and 15 of Ogihara et al.), for example, which are located immediately proximate the fuel spray. A similar understanding of the term "nozzle" to that described herein is used in U.S. Pat. No. 5,127,156 (Yokoyama et al.) to Hitachi, Ltd. (Ibaraki, Japan). There, the nozzle **10** is defined separately from elements of the attached and integrated structure, such as "swirler" **12** (see FIG. **1**(II)). The above-defined understanding should be understood when the term "nozzle" is referred to throughout the remainder of the description and claims.

In some cases, a disclosed microstructure can be a three-dimensional rectilinear body such as a polyhedron, such as a tetrahedron or a hexahedron, a prism, or a pyramid, or a portion, or a combination, of such bodies, such as a frustum. For example, FIG. **2** is a schematic three-dimensional view of a microstructure **220** that is disposed on a substrate **210** and includes a planar or flat base **230**, a planar or flat top **240** and a side **250** that connects the top to the base. Side **250** includes a plurality of planar or flat facets, such as facets **260**, **265** and **270**. Microstructure **220** can be used as a mold to fabricate holes for use in, for example, a nozzle.

In some cases, a disclosed microstructure can be a three-dimensional curvilinear body or a portion of such body, such as a segment of a sphere, an asphere, an ellipsoid, a spheroid, a paraboloid, a cone or a truncated cone, or a cylinder. For example, FIG. **3** is a schematic three-dimensional view of a microstructure **320** that is disposed on a substrate **310** and includes a planar or flat base **330**, a planar or flat top **340** and a curvilinear side **350** that connects the top to the base. In the exemplary microstructure **320**, top **340** and base **330** have the same shape. Microstructure **320** tapers narrower from base **330** to top **340**. As a result, top **340** has a smaller area than base **330**. Microstructure **320** can be used as a mold to fabricate holes for use in, for example, a nozzle.

In some cases, some of the characteristics of a disclosed microstructure changes from the base to the top. For example, in some cases, a disclosed microstructure can be a tapered microstructure. For example, FIG. **4** is a schematic three-dimensional view of a microstructure **420** that can be fabricated using a multiphoton process. Microstructure **420** can be used as a mold to fabricate holes for use in, for example, a nozzle. Microstructure **420** is disposed on a substrate **410** and includes a base **430**, a top **440**, and a side **450** connecting the top to the base. Microstructure **420** has a height or thickness h_1 which is the distance between base **430** and top **440** along the z-axis. Microstructure **420** is tapered. In particular, the cross-sectional area of the microstructure along the thickness of the microstructure decreases from base **430** to top **440**. For example, microstructure **420** includes a cross-section **460** at height h_2 in the xy-plane and a cross-section **470** at height $h_3>h_2$ in the xy-plane. The area of cross-section **470** is less than the area of cross-section **460**, and the area of cross-section **460** is less than the area of base **430**.

Base **430** has a first shape and top **440** has a second shape that is different than the first shape. In some cases, the first shape is an elliptical shape and the second shape is a circular shape. For example, FIG. **5** is a schematic three-dimensional view of a microstructure **520** that includes an elliptical base **530**, a circular top **540**, and a side **550** that connects the top to the base. Elliptical base **530** has a major axis **560** along the y-direction having a length "a" and a minor axis **570** along the x-direction having a length "b" different than "a". Circular top **540** has a radius r. Microstructure **520** is tapered. In particular, the area of circular top **540** is less than the area of elliptical base **530**.

As another example, the first shape can be a racetrack and the second shape can, for example, be a circle. For example, FIG. **6** is a schematic of a base **630** that can be the base of a disclosed microstructure. Base **630** includes two circles **642** and **644** and a middle portion **650**. Base **630** has a perimeter **660** that includes curved portions or arcs **632** and **634** and linear portions **636** and **638**. Curved portions **632** and **634** are portions of respective circles **642** and **644**.

In some cases, a disclosed microstructure has a cross-section along the thickness or height direction of the microstructure that rotates from the base of the microstructure to the top of the microstructure. For example, FIG. **7** is a schematic three-dimensional view of a microstructure **720** that includes a base **730** disposed in the xy-plane, a top **740** disposed in the xy-plane, and a side **780** that connects the top to the base. Microstructure **720** has a height h_4. Microstructure **720** has an xy cross-section that rotates clockwise from top **740** to base **730**. In particular, top **740** has an axis of symmetry **742** along the x-direction, an xy cross-section **750** of the microstructure at a height $h_5<h_4$ has an axis of symmetry **752** that is rotated clockwise relative to axis of symmetry **742**, an xy cross-section **755** of the microstructure at a height $h_6<h_5$ has an axis of symmetry **757** that is rotated clockwise relative to axis of symmetry **752**, an xy cross-section **760** of the microstructure at height a $h_7<h_6$ has an axis of symmetry **762** that is rotated clockwise relative to axis of symmetry **757**, and base **730** has an axis of symmetry **732** along the y-axis that is rotated clockwise relative to axis of symmetry **762**. Equivalently, microstructure **720** has an xy cross-section that rotates counter clockwise from base **730** to top **740**. FIG. **8** is a schematic top-view of microstructure **720** illustrating top **740** and its axis of symmetry **742**, cross-section **750** and its axis of symmetry **752**, cross-section **755** and its axis of symmetry **757**, cross-section **760** and its axis of symmetry **762**, and base **730** and its axis of symmetry **732**. Viewed from the top, the axes of symmetry of the cross-sections rotate clockwise from the top to the base. Such a rotation results in a twist in the microstructure along its height or thickness. In some cases, each cross-section can be an ellipse with a corresponding major axis acting as an axis of symmetry. In such cases, the major axis rotates from the base to the top. In some cases, such as when the microstructure is tapered and twisted, the cross-sections rotate and become smaller from the base to the top. For example, an elliptical base **730** has a major axis **732** along the y-direction having a length "a" and a minor axis **734** along the x-direction having a length "b" different than "a". As the major axis rotates from the base to the top, the ratio a/b is reduced by, for example, decreasing "a" resulting in a smaller ellipse that eventually can become a circle at the top (a=b). In general, a disclosed microstructure can include a taper and/or a twist or spiral along the thickness of the microstructure from the base to the top.

Microstructure **720** can be used as a mold to fabricate one or more holes in a nozzle with the holes having substantially the same profile as microstructure **720**. For example, the fabrication results in a hole **720** having a hole entry **730**, a hole exit **740** and a wall **752** extending from the hole entry to the hole exit. The hole tapers and spirals or twists from the hole entry to the hole exit. A disclosed spiraling or twisting nozzle hole can advantageously be used in a fuel injector to enhance the flow velocity of the fuel, reduce droplet size, and improve the mixing of fuel with air.

The microstructure may be understood as having a "diameter" at different heights of the microstructure (e.g. h_6, h_5, etc.). The diameter may be understood as the maximum distance between the edges of the microstructure at a common height. In the situation, where there is an elliptical base, such as at hole entry **730**, the diameter will be the distance between the edges of the microstructure along the major axis **732**. At the opposite end of the structure, corresponding to hole exit **740**, the diameter will similarly be the maximum distance between the edges of the microstructure at the common height (here, h_4). Thus, the distance between the edges of the microstructure along axis **742** will correspond to the diameter of the hole exit. In some embodiments the hole entry may have a diameter of less than 300 microns, or of less than 200 microns, or of less than or equal to 160 microns, or of less than 140 microns. In some embodiments the hole exit may have a diameter of less than 300 microns, or less than 200 microns, or less than 100 microns, or less than or equal to 40 microns, or less than 25 microns.

In some cases, the cross-section of nozzle hole **720** has an increasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section of nozzle hole **720** has a decreasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section has a constant rotation rate from the hole entry to the hole exit.

In general, a base or a lateral cross-section of a disclosed microstructure, or an entry hole or a lateral cross-section of a disclosed nozzle hole, can have any cross-section that may be desirable in an application. In some cases, the base or the entry hole can have a perimeter that includes the outer arcs of closely packed circles, where the outer arcs are connected by curve-like fillets. For example, FIG. **9** is a schematic three-dimensional view of a microstructure **920** that includes a base **930**, a top **940**, and a side **950** that connects the base to the top. FIG. **10** is a schematic of base **930** having a perimeter **1090** that includes the outer arcs of four closely packed circles, where the outer arcs are connected by curve-like fillets. In particular, perimeter **1090** includes an outer arc **1010** of a circle **1020**, an outer arc **1012** of a circle **1022**, an outer arc **1011** of a circle **1024**, and an outer arc **1016** of a circle **1026**, where outer arcs **1010** and **1012** are connected by curve-like fillet **1030**, outer arcs **1012** and **1014** are connected by curve-like fillet **1032**, outer arcs **1014** and **1016** are connected by curve-like fillet **1034**, and outer arcs **1016** and **1010** are connected by curve-like fillet **1036**. Circles **1010**, **1012**, **1014** and **1016** form a square array of equal and touching circles where each circle has a radius r_1.

Base **930** includes an axis of symmetry **1040**. The lateral cross-sections of microstructure **920** rotate and the radius r_1

decreases from base **930** to top **940** resulting in a microstructure that spirals and tapers narrower from base **930** to top **940**.

Equivalently, a nozzle hole **920** includes a hole entry **930**, a hole exit **940** and a wall **950** extending from the hole entry to the hole exit. Hole **920** has a lateral cross-section that rotates and becomes smaller from the hole entry to the hole exit.

FIG. **11** is a schematic top-view of nozzle hole (or microstructure) **920** illustrating hole entry **930** having axis of symmetry **1040** and hole exit **940** having axis of symmetry **942**. Viewed from the top, the axes of symmetry of the cross-sections of hole **920** rotate counter clockwise from the hole entry to the hole exit. Such a rotation results in a twist in the hole along its height or thickness.

As another example, FIG. **12** is a schematic three-dimensional view of a nozzle hole (or microstructure) **1220** that has a height k_1 and includes a hole entry **1230**, a hole exit **1240**, and a wall **1250** that extends from the hole entry to the hole exit. FIG. **13** is a schematic of hole entry **1230** having a perimeter **1235** that includes the outer arcs of two closely packed or touching circles, where the outer arcs are connected by curve-like fillets. In particular, perimeter **1090** includes an outer arc **1270** of a circle **1280** and an outer arc **1272** of a circle **1282**, where each circle has a radius r_2 and outer arcs **1270** and **1272** are connected by curve-like fillets **1290** and **1292**.

Hole entry **1230** includes an axis of symmetry **1232**. The lateral cross-sections of nozzle hole **1220** rotate and the radius r_2 decreases from hole entry **1230** to hole exit **1240** resulting in a microstructure that spirals and tapers narrower from hole entry **1230** to hole exit **1240**. In particular, top **1240** has an axis of symmetry **1242** along the x-direction, an xy cross-section **1264** of the hole at a height $k_2<k_1$ has an axis of symmetry **1265** that is rotated clockwise relative to axis of symmetry **1242**, an xy cross-section **1262** of the hole at a height $k_3<k_2$ has an axis of symmetry **1263** that is rotated clockwise relative to axis of symmetry **1265**, an xy cross-section **1260** of the hole at a height $k_4<k_3$ has an axis of symmetry **1261** that is rotated clockwise relative to axis of symmetry **1263**, and hole entry **1230** has an axis of symmetry **1232** along the y-axis that is rotated clockwise relative to axis of symmetry **1261**. Hence, hole **1220** has an xy cross-section that rotates clockwise from hole exit **1240** to hole entry **1230**. Equivalently, hole **1220** has an xy cross-section that rotates counter clockwise from the hole entry to the hole exit. FIG. **14** is a schematic top-view of nozzle hole **1220** illustrating hole exit **1242** and its axis of symmetry **1242** along the x-axis, cross-section **1264** and its axis of symmetry **1265**, cross-section **1262** and its axis of symmetry **1263**, cross-section **1260** and its axis of symmetry **1261**, and hole entry **1230** and its axis of symmetry **1232** along the y-axis. Viewed from the top, the axes of symmetry of the lateral cross-sections of the hole rotate clockwise from the hole exit to the hole entry.

Equivalently, a microstructure **1220** includes a base **1230**, a top **1240** and a side **1250** that connects the base to the top. Microstructure **1220** has a cross-section that rotates and becomes smaller from the base to the top.

As shown in FIGS. **2** through **14**, the microstructures disclosed herein that serve as nozzles may be monolithic structures. In other words, the microstructures **220**, **320**, **420** etc. that forms the actual nozzles are created from, and ultimately form a common, single piece of material. This may be understood as different from nozzles that are formed through a combination of a number of different parts, where such parts are potentially made up of different materials. In this regard, as shown in the above-mentioned figures, the nozzles disclosed herein may be monolithic structures.

In general, a plurality of disclosed microstructures or holes can have any arrangement that may be desirable in an application. For example, in some cases, the disclosed holes can be arranged regularly or irregularly. For example, FIG. **15**A is a schematic top-view of a two-dimensional square array **1500** of holes or microstructures **1510**, and FIG. **15**B is a schematic top-view of a two-dimensional hexagonal array **1520** of holes or microstructures **1530**, where holes or microstructures **1510** and **1530** can be any nozzle hole or microstructure disclosed herein. In some cases, a plurality of disclosed microstructures or hole may be arranged on a non-planar surface. For example, FIG. **16** is a schematic three-dimensional view of a plurality of nozzle holes or microstructures **1610** disposed or arranged on a spherical surface **1620**.

In some cases, a disclosed microstructure or hole may have one or more fillets for ease of manufacturing and/or to reduce local stress. For example, FIG. **17** is a schematic side-view of a microstructure **1720** that is disposed on a substrate **1710** and includes a base **1730**, a top **1740**, and a side **1750** connecting the base to the top. Microstructure **1720** includes fillets **1760** and **1761** smoothly joining side **1750** and top **1740**, and fillets **1770** and **1771** smoothly joining side **1750** and top surface **1705** of substrate **1710**.

The nozzle holes and microstructures disclosed herein can be fabricated using the method outlined in reference to FIGS. **1**A-**1**M. The method provides flexibility and control in producing a variety of individual microstructures and holes in a single array, yet can be used to achieve desirably low levels of average surface roughness while maintaining industrially acceptable fabrication speeds or "throughput."

FIG. **1**A is a schematic side-view of a layer **115** of a first material disposed on a substrate **110**. The first material is capable of undergoing multiphoton reaction by simultaneously absorbing multiple photons. For example, in some cases, the first material is capable of undergoing a two photon reaction by simultaneously absorbing two photons. The first material can be any material or material system that is capable of undergoing multiphoton, such as two photon, reaction, such as those describe in U.S. Pat. Nos. 7,583,444 and 7,941,013; and PCT Publication WO 2009/048705, "Highly Functional Multiphoton Curable Reactive Species," all of which are incorporated herein by reference.

In some cases, the first material can be a photoreactive composition that includes at least one reactive species that is capable of undergoing an acid- or radical-initiated chemical reaction, and at least one multiphoton photoinitiator system. Reactive species suitable for use in the photoreactive compositions include both curable and non-curable species. Exemplary curable species include addition-polymerizable monomers and oligomers and addition-crosslinkable polymers (such as free-radically polymerizable or crosslinkable ethylenically-unsaturated species including, for example, acrylates, methacrylates, and certain vinyl compounds such as styrenes), as well as cationically-polymerizable monomers and oligomers and cationically-crosslinkable polymers (which species are most commonly acid-initiated and which include, for example, epoxies, vinyl ethers, cyanate esters, etc.), and the like, and mixtures thereof. Exemplary non-curable species include reactive polymers whose solubility can be increased upon acid- or radical-induced reaction. Such reactive polymers include, for example, aqueous insoluble polymers bearing ester groups that can be converted by photogenerated acid to aqueous soluble acid groups (for example, poly(4-tert-butoxycarbonyloxystyrene). Non-curable species also include the chemically-amplified photoresists.

The multiphoton photoinitiator system enables polymerization to be confined or limited to the focal region of a focused beam of light used to expose the first material. Such a system preferably is a two- or three-component system that includes at least one multiphoton photosensitizer, at least one photoinitiator (or electron acceptor), and, optionally, at least one electron donor.

Layer **115** of the first material can be coated on substrate **110** using any coating method that may be desirable in an application. For example, the first material can be coated on substrate **110** by flood coating. Other exemplary coating methods include knife coating, notch coating, reverse roll coating, gravure coating, spray coating, bar coating, spin coating and dip coating.

Substrate **110** can be chosen from a wide variety of films, sheets, and other surfaces (including silicon wafers and glass plates), depending upon the particular application and the method of exposure to be utilized. In some cases, substrate **110** is sufficiently flat so that layer **115** of the first material has a uniform thickness. In some cases, layer **115** can be exposed in bulk form. In such cases, substrate **110** may be excluded from the fabrication process. In some cases, such as when the process includes one or more electroplating steps, substrate **110** can be electrically conductive or semi-conductive.

Next, the first material is selectively exposed to an incident light having sufficient intensity to cause simultaneous absorption of multiple photons by the first material in the exposed region. The exposure can be accomplished by any method that is capable of providing light with sufficient intensity. Exemplary exposure methods are described in U.S. Pat. No. 8,858,807, which is incorporated herein by reference.

FIG. **18** is a schematic side-view of an exemplary exposure system **1800** for exposing layer **115** of the first material. The exposure system includes a light source **1820** emitting light **1830** and a stage **1810** that is capable of moving in one, two, or three dimensions. Substrate **110** coated with layer of first material **115** is placed on the stage. Optical system **1840** focuses emitted light **1830** at a focal region **1850** within the first material. In some cases, optical system **1840** is designed so that simultaneous absorption of multiple photons by the first material occurs only at or very near focal region **1850**. Regions of layer **115** that undergo the multiphoton reaction become more, or less, soluble in at least one solvent compared to regions of layer **115** that do not undergo the multiphoton reaction.

Focal region **1850** can scan a three-dimensional pattern within the first material by moving stage **1810** and/or light **1830** and/or one or more components, such as one or more mirrors, in optical system **1840**. In the exemplary process illustrated in FIGS. **1**A and **18**, layer **115** is disposed on a planar substrate **110**. In general, substrate **110** can have any shape that may be desirable in an application. For example, in some cases, substrate **110** can have a spherical shape.

Light source **1820** can be any light source that is capable of producing sufficient light intensity to effect multiphoton absorption. Exemplary light sources include lasers, such as femtosecond lasers, operating in a range from about 300 nm to about 1500 nm, or from about 400 nm to about 1100 nm, or from about 600 nm to about 900 nm, or from about 750 to about 850 nm.

Optical system **1840** can include, for example, refractive optical elements (for example, lenses or microlens arrays), reflective optical elements (for example, retroreflectors or focusing mirrors), diffractive optical elements (for example, gratings, phase masks, and holograms), polarizing optical elements (for example, linear polarizers and waveplates), dispersive optical elements (for example, prisms and gratings), diffusers, Pockels cells, waveguides, and the like. Such optical elements are useful for focusing, beam delivery, beam/mode shaping, pulse shaping, and pulse timing.

After selective exposure of layer **115** of the first material by exposure system **1800**, the exposed layer is placed in a solvent to dissolve regions of higher solvent solubility. Exemplary solvents that can be used for developing the exposed first material include aqueous solvents such as, for example, water (for example, having a pH in a range of from 1 to 12) and miscible blends of water with organic solvents (for example, methanol, ethanol, propanol, acetone, acetonitrile, dimethylformamide, N-methylpyrrolidone, and the like, and mixtures thereof); and organic solvents. Exemplary useful organic solvents include alcohols (for example, methanol, ethanol, and propanol), ketones (for example, acetone, cyclopentanone, and methyl ethyl ketone), aromatics (for example, toluene), halocarbons (for example, methylene chloride and chloroform), nitriles (for example, acetonitrile), esters (for example, ethyl acetate and propylene glycol methyl ether acetate), ethers (for example, diethyl ether and tetrahydrofuran), amides (for example, N-methylpyrrolidone), and the like, and mixtures thereof. FIG. **1**B is a schematic side-view of a first microstructured pattern **121** formed in the first material using the multiphoton process. The first microstructured pattern includes a first cluster **122** of microstructures **120** and a second cluster **124** of microstructures **125**, where microstructures **120** and **125** can be any microstructures including any microstructures disclosed herein. In some cases, microstructures **120** and **125** have different structures. In some cases, microstructures **120** and **125** have the same structure. In the exemplary first microstructured pattern **121**, microstructures **120** and **125** have heights t_1.

FIGS. **19** and **20** are scanning electron micrographs of a cluster of microstructures **120** fabricated according to the processes disclosed herein. The microstructures in FIGS. **19** and **20** are similar to microstructures **1220** shown in FIG. **12**. In FIG. **19**, the microstructures are viewed along the minor axes of the bases of the microstructures and in FIG. **20**, the microstructures are viewed along the major axes of the bases of the microstructures.

The plurality of microstructures in FIG. **19** (and FIG. **20**) are arranged in an array of concentric circles that includes an outermost circle **1910**. The microstructures are arranged such that no diameter of the outermost circle includes at lease one discrete microstructure from each circle in the array of concentric circles. For example, a diameter **1920** of outermost circle **1910** includes microstructures **1901-1905** but not microstructures **1930** and **1931**. Each circle in the array of concentric circles in FIG. **19** includes equally spaced discrete microstructures. Similarly, in some cases, a nozzle includes a plurality of holes that are arranged in an array of concentric circles that includes an outermost circle. The discrete nozzle holes are arranged such that no diameter of the outermost circle includes at lease one discrete nozzle hole from each circle in the array of concentric circles. In some cases, each circle in the array of concentric circles comprises equally spaced discrete nozzle holes.

Next, as schematically illustrated in FIG. **1**C, top surface **126** of first microstructured pattern **121** is metalized or made electrically conductive by coating the top surface with a thin electrically conductive seed layer **127**. Conductive seed layer **127** can include any electrically conductive material that is desirable in an application. Exemplary conductive materials include silver, chromium, gold and titanium. In some cases, seed layer **127** has a thickness that is less than about 50 nm, or less than about 40 nm, or less than about 30 nm, or less than about 20 nm.

Next, as schematically illustrated in FIG. **1**D, seed layer **127** is used to electroplate first microstructured pattern **121** with a second material resulting in a layer **130** of the second material. In some cases, the electroplating of first microstructured pattern **121** is continued until the minimum thickness t**2** of layer **130** is greater than t_1.

Suitable second materials for electroplating include silver, passivated silver, gold, rhodium, aluminum, enhanced reflectivity aluminum, copper, indium, nickel, chromium, tin, and alloys thereof.

In some cases, layer **130** of the second material has an uneven or rough top surface **132**. In such cases, layer **130** of the second material is polished or ground resulting in a layer **135** of the second material having a thickness $t_3>t_1$ as illustrated schematically in FIG. **1**E. The grinding or polishing can be accomplished using any grinding method that may be desirable in an application. Exemplary grinding methods include surface grinding and mechanical milling.

In some cases, layer of second material **130** can be directly deposited on first microstructured pattern **121** without first coating pattern **121** with seed layer **127**. In such cases, layer **130** can be coated on pattern **121** by any using suitable method including, for example, sputtering and chemical vapor deposition.

Next, substrate **110** and the first material are removed resulting in a first mold **140** of the second material shown schematically in FIG. **1**F. For ease of viewing and without loss of generality, seed layer **127** is not shown in FIG. **1**F. In some cases, substrate **110** and the patterned first material can be separated from layer **135** by hand. In some cases, the separation can be carried out prior to grinding layer **130**.

First mold **140** includes a second microstructured pattern **141** that is substantially the negative replica of first microstructured pattern **121**. In particular, first mold **140** of the second material includes a first cluster **146** of microstructures **145** and a second cluster **147** of microstructures **148**, where microstructures **145** are substantially negative replicas of microstructures **120** and microstructures **148** are substantially negative replicas of microstructures **125**.

Next, the second microstructured pattern is replicated in a third material **150** different than the first and second materials by disposing the third material in between first mold **140** of the second material and a substrate **155** having a smooth top surface **157** as schematically illustrated in FIG. **1**G. The replication process can be accomplished using any suitable replication method. For example, in some cases, the replication can be accomplished by using an injection molding process. In such cases, a molten third material **150** can be introduced between substrate **155** and first mold **140** and solidified after the molten third material fills the second microstructured pattern. The third material **150** can be any material that is capable of replicating a pattern. Exemplary third materials include polycarbonate and other thermoplastics such as polystyrene, acrylic, styrene acrylonitrile, polymethyl methacrylate (PMMA), cyclo olefin polymer, polyethylene terephthalate, polyethylene 2,6-naphthalate, and fluoropolymers.

After the replication process, first mold **140** of the second material and substrate **155** are removed resulting in a second mold **160** of the third material having a substrate portion **162** and a third microstructured pattern **161** that is substantially the negative replica of second microstructured pattern **141** and substantially a positive replica of first microstructured pattern **121**. Third microstructured pattern **161** includes a first cluster **168** of microstructures **165** and a second cluster **169** of microstructures **159**, where microstructures **165** are substantially negative replicas of microstructures **145** and microstructures **159** are substantially negative replicas of microstructures **148**. In some cases, microstructures **165** are substantially positive replicas of microstructures **120** and microstructures **159** are substantially positive replicas of microstructures **125**. FIG. **21** is a scanning electron micrograph of a cluster of polycarbonate microstructures **165** fabricated according to the processes disclosed herein.

Next, as schematically illustrated in FIG. **1**I, top surface **154** of third microstructured pattern **161** is metalized or made electrically conductive by coating the top surface with a thin electrically conductive seed layer **167** similar to seed layer **127**.

Next, as schematically illustrated in FIG. **1**J, seed layer **167** is used to electroplate third microstructured pattern **161** with a fourth material different than the third material resulting in a layer **170** of the fourth material. In some cases, the electroplating of second microstructured pattern **161** is continued until the minimum thickness t_5 of layer **130** is greater than t_4, the height of the microstructures in second mold **160**. In some cases, height t_4 is substantially equal to height t_1. Suitable fourth materials for electroplating include silver, passivated silver, gold, rhodium, aluminum, enhanced reflectivity aluminum, copper, indium, nickel, chromium, tin, and alloys thereof. In other embodiments, the fourth material may be a ceramic that is deposited on third microstructured pattern. Such a ceramic material may be formed, e.g., by a sol-gel process as described in commonly owned and assigned U.S. Pat. No. 5,453,104, or by photocuring of a ceramic-filled or pre-ceramic polymeric composition as described in commonly owned and assigned U.S. Pat. Nos. 6,572,693, 6,387,981, 6,899,948, 7,393,882, 7,297,374, and 7,582,685, each of which is herein incorporated by reference in its entirety. Such ceramic materials may comprise, e.g., silica, zirconia, alumina, titania, or oxides of yttrium, strontium, barium, hafnium, niobium, tantalum, tungsten, bismuth, molybdenum, tin, zinc, lanthanide elements (i.e. elements having atomic numbers ranging from 57 to 71, inclusive), cerium and combinations thereof.

Next, top surface of **172** of layer **170** is ground until tops **171** of microstructures **165** and tops **173** of microstructures **159** are exposed. In some cases, the third material is softer than the fourth material. For example, in some cases, the third material is polycarbonate and the fourth material is a nickel alloy. In such cases, small portions of tops **171** and **173** can be removed during the grinding process to ensure that the tops of all the microstructures in third microstructured pattern **161** are exposed. In such cases, the grinding results, as schematically illustrated in FIG. **1**K, in a layer **175** of the fourth material planarizing the third microstructured pattern and exposing tops **185** of the microstructures in the plurality of microstructures in the third microstructured pattern. Layer **175** of the fourth material has a top surface **177** that is substantially even with tops **184** of microstructures **180** and tops **186** of microstructures **181**. The microstructures have a height t_6 that can be slightly less than t_4.

Next, second mold **160** is removed resulting in a layer **190** of the fourth material that includes a plurality of holes **106** that correspond to the plurality of microstructures in third microstructured pattern **161**. In particular, layer **190** of the fourth material includes a first cluster **192** of holes **195** and a second cluster **193** of holes **198**. In some cases, holes **195** are substantial replicas of microstructures **120** and holes **198** are substantial replicas of microstructures **125**. Holes **195** include hole entries **182** and hole exits **183** and holes **198** include hole entries **196** and hole exits **197**.

FIGS. **22** and **23** are optical micrographs of respective hole entries **182** and hole exits **183** of a cluster **192** of holes **195** made according to the processes disclosed herein. FIG. **25** is a scanning electron micrograph of one of the holes **195**, viewed from the hole entry side. The hole has a hole entry **2510** and a hole exit **2520** that is smaller than the hole entry. The micrograph clearly illustrates a taper and a twist in the hole.

In some cases, two clusters **192** and **193** are separated along a direction **199** resulting, as illustrated schematically in FIG. **1M**, in a part **102** and a separate, and in some cases substantially identical, part **103**, where each part can be used in a spray nozzle and/or a fuel injector.

FIG. **24** is a schematic side-view of a nozzle **2400** that includes a hollow interior **2410** and a wall **2405** separating the hollow interior from an outside **2430** of the nozzle. The nozzle further includes at least one hole, such as a hole **2420**, that connects hollow interior **2410** to outside **2430** of the nozzle. The holes deliver gas or liquid from the hollow interior to the outside. Hole **2420** can be any hole disclosed herein. Hole **2420** includes a hole entry **2440** at an inner surface **2406** of wall **2405** and a hole exit **2445** at an outside surface **2407** of wall **2405**. Hole entry **2440** is also at hollow interior **2410** of the nozzle and hole exit **2445** is at outside **2430** of the nozzle.

In some cases, hole entry **2440** has a first shape and hole exit **2445** has a second shape that is different than the first shape. For example, in some cases, the first shape is an elliptical shape and the second shape is a circular shape. As another example, in some cases, the first shape can be a racetrack shape and the second shape can be a circular shape. As another example, in some cases, the second shape can be a circle or an ellipse and the perimeter of the first shape can include outer arcs of a plurality of closely packed circles, where the outer arcs are connected to each other by curve-like fillets.

In some cases the first shape can be substantially the same as the second shape, but they can have different magnifications or sizes. For example, the first shape can be a circle with a radius a_1 and the second shape can also be a circle, but with a radius a_2 different than a_1.

In some cases, hole **2420** has a lateral cross-section that rotates from hole entry **2440** to hole exit **2445** where lateral cross-section refers to a cross-section that is substantially perpendicular to the general flow direction of, for example, a liquid or gas within the hole. In some cases, the cross-section has an increasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section has a decreasing rotation rate from the hole entry to the hole exit. In some cases, the cross-section has a constant rotation rate from the hole entry to the hole exit.

Some of the advantages of microstructures, holes, layers, constructions, and methods of this invention are further illustrated by the following example. The particular materials, amounts and dimensions recited in the example, as well as other conditions and details, should not be construed to unduly limit this invention. Unless otherwise noted, all chemical procedures were carried out under a dry nitrogen atmosphere with dry and deoxygenated solvents and reagents. Unless otherwise noted, all solvents and reagents were or can be obtained from Aldrich Chemical Co., Milwaukee, Wis.

Rhodamine B hexafluoroantimonate was prepared by metathesis of Rhodamine B chloride with sodium hexafluoroantimonate. As used herein, SR368 refers to tris-(2-hydroxyethyl)isocyanurate triacrylate, (obtained from Sartomer Co. Inc., Exton, Pa.; SR9008 refers to a trifunctional acrylate ester (obtained from Sartomer); SR1012 refers to diaryliodonium hexafluoroantimonate (obtained from Sartomer); SU-8 R2150 refers to an epoxy negative photoresist (obtained from MicroChem Corp., Newton, Mass.); THF refers to tetrahydrofuran; LEXAN HPS1R refers to a thermoplastic polycarbonate (obtained from Sabic Innovative Plastics, Pittsfield, Mass.; and Inco S-Rounds refers to nickel (obtained from Vale Inco America's, Inc., Saddle Brook, N.J.).

Example 1

A circular silicon wafer (substrate **110** in FIG. **1A**), 10.2 cm in diameter, was obtained from Wafer World, Inc., West Palm Beach, Fla. The Si wafer was cleaned by soaking it for approximately ten minutes in a 3:1 mixture by volume of concentrated sulfuric acid and 30% by weight aqueous hydrogen peroxide. The wafer was then rinsed with deionized water and then with isopropanol, after which it was dried under a stream of air. The wafer was then dipped into a two weight percent solution of 3-(trimethoxysilyl)propyl methacrylate in 190-proof ethanol that had been made acidic (pH between 4 and 5) with acetic acid. The wafer was then rinsed with absolute ethanol and was then heated in an oven at 130° C. for ten minutes.

Poly(methyl methacrylate), having a number average molecular weight of approximately 120,000, SR9008, and SR368 were combined in a weight ratio of 30:35:35 resulting in a monomer mixture that was dissolved in sufficient 1,2-dichloroethane to afford a solution that was 54 weight percent of the monomer mixture. To this solution there were then added aliquots of concentrated solutions of photosensitizer Rhodamine B hexafluoroantimonate in THF and SR1012 in THF sufficient to give a coating solution that was 0.5 weight percent Rhodamine B hexafluoroantimonate and 1.0 weight percent SR1012, based on the total weight of solids. This coating solution was filtered through a 1-micron syringe filter and was spin-coated onto the silicon wafer. The coated wafer was placed in a forced air oven at 60° C. for 18 hours to afford a coated silicon wafer with a substantially solvent-free (hereinafter, "dry") coating (layer **115** of the first material in FIG. **1A**) having a thickness of approximately 300 μm.

Two-photon polymerization of the dry coating was carried out using a diode-pumped Ti:sapphire laser (obtained from Spectra-Physics, Mountain View, Calif.) that operated at 800 nm with a nominal pulse width of 80 fs, a pulse repetition rate of 80 MHz, and an average power of approximately 1 W. The coated wafer was placed on a computer-controlled three-axis stage (obtained from Aerotech, Inc., Pittsburgh, Pa.). The laser beam was attenuated by neutral density filters and was focused into the dry coating using a galvoscanner with a telescope for x-, y-, and z-axis control (available from Nutfield Technology, Inc., Windham, N.H.). A Nikon CFI Plan Achromat 50× oil objective N.A. 0.90 with a working distance of 0.400 mm and a 4.0 mm focal length was applied directly onto the surface of the dry coating. The average power was measured at the output of the objective lens using a wavelength-calibrated photodiode (obtained from Ophir Optronics, Ltd., Wilmington, Mass.) and was determined to be approximately 8 mW.

After the exposure scan was completed, the exposed dry coating was developed in MicroChem SU-8 solvent, rinsed and dried resulting in a first microstructured pattern **121** (FIG. **1***b*).

The surface of the first microstructured pattern was made conductive by sputtering a thin layer (about 100 angstroms) of Silver (Ag) on the surface of the pattern. The metalized front surface was then electroplated with Inco S-Rounds (nickel) until it was approximately 2 mm thick. The electroplated nickel slug was then separated from the first pattern and ground and machined resulting in a first mold **140** having a second microstructured pattern **141** (FIG. **1**F).

The first mold was then placed into an injection die mold which was placed into a single screw plastic injection molding system to inject thermoplastic polycarbonate (LEXAN HPS1R) into the mold cavity resulting in a second mold **160** having a third microstructured pattern **161** (FIG. **1**H).

The front surface of the second mold was then metalized by sputtering the surface with about 100 angstroms of silver. The metalized second mold was then electroplated with Inco S-Rounds (nickel) to totally cover the third microstructured pattern resulting in a nickel layer **170** (FIG. **1**J).

After rinsing the combined construction of the nickel layer and the second mold with deionized water, the front surface **172** (FIG. **1**J) of the nickel layer was ground in a planar fashion to remove the nickel material from the tops **171** of the third microstructured pattern.

After the grinding was complete (all the microstructure tops were exposed), the electroplated nickel layer was separated from the polycarbonate mold **160** resulting in a nickel disc, approximately 8 mm in diameter and 160 um thick having 37 through-holes arranged in a circular hexagonal packing arrangement. The separation between neighboring holes was about 200 μm. Each hole had a hole entry in the shape of a racetrack modified with fillets along the linear portions of the racetrack. The racetrack had a major diameter of about 80 μm and a minor diameter of about 50 μm. Each hole had a hole exit in the shape of a smaller racetrack with a major diameter of about 50 μm and a minor diameter of about 35 μm. Viewed from the hole exit side, the major diameters of the cross-section of the holes rotated clockwise from the hole exit to the hole entry by about 30 degrees for every 50 μm of depth below the hole exit.

As used herein, terms such as “vertical”, “horizontal”, “above”, “below”, “left”, “right”, “upper” and “lower”, “clockwise” and “counter clockwise” and other similar terms, refer to relative positions as shown in the figures. In general, a physical embodiment can have a different orientation, and in that case, the terms are intended to refer to relative positions modified to the actual orientation of the device. For example, even if the image in FIG. **1**B is flipped as compared to the orientation in the figure, surface **126** is still considered to be the top surface.

All patents, patent applications, and other publications cited above are incorporated by reference into this document as if reproduced in full. While specific examples of the invention are described in detail above to facilitate explanation of various aspects of the invention, it should be understood that the intention is not to limit the invention to the specifics of the examples. Rather, the intention is to cover all modifications, embodiments, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A fuel injector nozzle comprising a plurality of holes formed therethrough connecting one side of the nozzle with an opposite side of the nozzle, each of the holes comprising:

a hole entry on the one side of the nozzle having a first shape;

a hole exit on the opposite side of the nozzle having a second shape, with the first shape being different than the second shape in size or shape or both size and shape;

an axis of symmetry passing from the hole entry to the hole exit; and

a hole wall connecting the hole entry to the hole exit, with the hole wall comprising a side that is continuously curved from the hole entry to the hole exit,

wherein a) at least one of the holes of the nozzle has a perimeter of the first shape of the hole entry comprise outer arcs of closely packed circles, with the outer arcs being connected by curve-like fillets and each circle having a different center point, or b) for at least one of the holes of the nozzle, the axis of symmetry passing from the hole entry to the hole exit is straight and the hole wall twists around the straight axis of symmetry.

2. The nozzle of claim **1**, wherein the hole wall tapers from the hole entry to the hole exit, for at least one of the holes of the nozzle.

3. The nozzle of claim **2**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight and the hole wall twists around the straight axis of symmetry, for at least one of the holes of the nozzle.

4. The nozzle of claim **1**, wherein the nozzle is a nozzle plate with the one side and the opposite side being parallel to each other.

5. The nozzle of claim **1**, wherein the hole wall comprises opposite sides that are both continuously curved from the hole entry to the hole exit, for at least one of the holes of the nozzle.

6. The nozzle of claim **1**, wherein the one side of the nozzle defines a hollow interior.

7. The nozzle of claim **1**, wherein the hole exit has a smaller area than that of the hole entry, for at least one of the holes of the nozzle.

8. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and at least one of the holes of the nozzle has the first shape be an elliptical shape and the second shape be a circular shape, for at least one of the holes of the nozzle.

9. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and at least one of the holes of the nozzle has the first shape be a racetrack shape and the second shape be a circular shape, for at least one of the holes of the nozzle.

10. The nozzle of claim **1**, wherein at least one of the holes of the nozzle has a perimeter of the first shape of the hole entry comprise outer arcs of closely packed circles, with the outer arcs being connected by curve-like fillets and each circle having a different center point.

11. A fuel injector comprising the nozzle of claim **1**.

12. An internal combustion engine comprising a fuel system comprising at least one fuel injector according to claim **11**.

13. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight and the hole wall twists around the straight axis of symmetry, for at least one of the holes of the nozzle.

14. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and the shape of the first shape is different than that of the second shape.

15. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and at least one of the holes of the nozzle has a cross-section that rotates at an increasing rotation rate from the hole entry to the hole exit.

16. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and at least one of the holes of the nozzle has a cross-section that rotates at a decreasing rotation rate from the hole entry to the hole exit.

17. The nozzle of claim **1**, wherein the axis of symmetry passing from the hole entry to the hole exit is straight, the hole wall twists around the straight axis of symmetry, and at least one of the holes of the nozzle has a cross-section that rotates at a constant rotation rate from the hole entry to the hole exit.

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